# THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE VAPOUR BY OXIDES AND MIXED OXIDES

BY

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SUMMARY

The vapour phase decomposition of hydrogen peroxide has been studied on a wide range of metal oxide, mixed oxide and promoted metal oxide surfaces. The investigation was conducted mainly in a flow system, in the temperature range 38 - 184°C using high-purity nitrogen as the carrier gas, and $H_2O_2$ partial pressures not greater than 1 mm of Hg. Oxide surfaces were held on vacuum flashed metal films, or "specpure" metal slips or else were presented to the gas stream as a compressed slip of the bulk oxide.

There have been many studies of $H_2O_2$ decomposition in solution but few in the vapour phase and these have been confined almost exclusively to work with inactive catalysts such as glass, $SiO_2$, $SnO_2$ and $Al_2O_3$. No difficulty was found in obtaining reproducible results with active oxides for the decomposition efficiency (D) and also for the temperature coefficient ($E_A$). On the basis of these two values the catalytic efficiencies of the oxides have been compared. In order of decreasing efficiency we find for single oxides:-

$Mn_2O_3 > PbO > Ag_2O > CoO/Co_2O_3 > Cu_2O > NiO$ "green" $> CuO >$

$Fe_2O_3 > CdO > ZnO = MgO > Sn\,O_2 > \alpha\text{-}Al_2O_3 >$ glass (pyrex)

This order taken in conjunction with the work of Garner, Stone, Wagner, Schwab and others on the decomposition of $N_2O$ and the combination of CO and $O_2$ leads us to classify the oxides on the tendency they exhibit to absorb or reject oxygen which is in turn related to the defect-type of the oxide.

We state then in the terminology of the semi-conductor field:-

p type (PbO, $Cu_2O$ etc.) > n-type (CuO, ZnO etc.) > insulators

Mg O, $\alpha$ - $Al_2O_3$) as catalysts.

The classification is examined with reference to the treatment of stoichiometric NiO with $Li_2O$ and $Ga_2O_3$, which produce strongly p-type and n-type oxide mixtures respectively. Two series of oxides mixed in stoichimetric proportion are also examined. These are the pre-spinel mixtures $Mn_2O_3/XO$, where X=Cd, Zn, Pb, Ni, and $CuO/Y_2O_3$ where Y=Al, Fe, Co. The effect of annealing temperature is carefully examined in the former case and it is shown that the best catalysts are those in which interdiffusion of ions has begun between oxide crystallites, but no stable spinel has yet formed. The most striking effects observed were in the synergesis obtained with the $Fe^{+++}$ and $Cu^{++}$ oxide mixture and the fact that inert ZnO seemed to promote the already extremely active $Mn_2O_3$.

On all catalysts, temperature coefficients were measured by making fast temperature changes. These values were, in most cases, dependant to some extent on the temperature from which the change was made - the higher temperature surface giving the highest temperature coefficient. Energies of activation calculated from temperature coefficients range from 4 - 34 K cals/mol.

Kinetic studies at constant temperatures on both p and n-type oxides viz:- $Fe_2O_3$, CoO, NiO yield:-

$$-\frac{d(p_{H_2O_2})}{dt} = K\frac{p_{H_2O_2}\cdot p_{O_2}^{1/8}}{p_{H_2O}^{1/2}}$$

A mechanism is put forward to explain this. It is suggested that catalysis depends on cyclic transfer of electrons between the surface and $H_2O_2$ or its radicals and ions. $O_2^-$ or $O^-$ adsorbed at p-type oxides (with attendant positive holes), or lattice oxygen vacancies (with attendant electrons)

in the surface of n-type oxides, are suggested as suitable sites for the catalytic cycle. Increase of oxygen pressure accelerated the catalysis both on n-type and p-type oxides - probably acting by raising the surface concentration of such species as $O_2^-$.

The catalyst surface is in slowly attained thermal equilibrium and also is subject to change with varying $H_2O_2$ pressure. These effects are observed and discussed.

To assess the possibility of linking the flow results with those of previous workers with static systems, a brief investigation has been conducted in a static apparatus. The conclusion is that comparison between static and dynamic systems is not easy to make.

Information on the physical properties of the oxide systems has been obtained from magnetic susceptibility, surface area and X-ray measurements. The significance of which is fully discussed.

GENERAL INTRODUCTION

There have been few investigations of the heterogeneous catalysis of hydrogen peroxide in the vapour phase. Those few have been conducted with relatively inert surfaces such as glass and aluminium. Yet there seems to be no inherent obstacle to the study by a flow method of the catalysis by a wide range of surfaces, including very active ones. Such a study would yield results of interest in the special field of $H_2O_2$ catalysis (So far studied in detail only in the aqueous phase.) and in the wider context of the general mechanism of catalysis.

The present work describes a study along these lines. It extends some earlier detailed work in this laboratory on one oxide, and considers variations in catalytic efficiency which are to be associated with chemical structure impurities, the defect structure of the solid, surface changes occuring during catalysis itself, and the effect of thermal pretreatment of the solid.

To begin with, a brief outline of past work on the decomposition of hydrogen peroxide in the liquid phase will be given. Since in that field much progress has been made towards a satisfactory understanding of the catalytic process. This will be followed by a section on previous vapour phase work with hydrogen peroxide; and a review of the defect structural properties of solid surfaces and bulk oxides, which have recently come to be recognised as being important in chemisorption and catalysis on oxides. In this connection an outline will be given of some fundamental studies on the solid oxide catalysed decomposition of $N_2O$ and of the $CO/O_2$ oxidation reaction which are clearly related to the present problem.

## (1) Catalytic Decomposition of Hydrogen Peroxide

### (a) Liquid Phase

Hydrogen Peroxide was discovered in 1818 by Louis - Jacques Thénard, who observed that it was rather unstable, presented a novel form of chemical combination and that it could be decomposed vigorously by certain substances without discernible effect on the decomposing agent (1,2) Between the date of his discovery and 1856, Thénard published upwards of thirty papers describing the properties and preparation of the compound. He also made comprehensive observations on the reactivity of $H_2O_2$ towards many metals and metallic oxides, including $Ag_2O$, $MnO_2$ and PbO, and noted that "in these decompositions, chemical action is evidently missing; it is necessary then to attribute these actions to a physical cause which might probably be electricity". This work of Thénards (3,4) constitutes one of the earliest recognitions of catalysis.

Since Thénard's early observations the advance of knowledge about hydrogen peroxide decomposition has been hindered by experimental difficulties. Much work was carried out with hydrogen peroxide of questionable purity. In many cases observations were not made in regard to the effects of concentration, temperature and the state of the catalyst.

The earliest systematic work on dilute aqueous solutions was reported in a long classical series of papers by Bredig (5), onwards from 1897. He used metal sols as catalysts which he recognised as being analogous in action to the biological enzyme, catalase. Bredig found that the

decomposition was first order in $H_2O_2$ concentration on most noble metal catalysts, and that there was an optimum rate at about pH 12. These general findings have been confirmed recently in detailed work by Teletof (6).

The basis of the early explanations of catalysis was an alternating oxidation - reduction cycle e.g. as proposed for catalysis by iodine:-

Oxidation: $2\ HI + H_2O_2 = I_2 + 2\ H_2O.$

Reduction: $I_2 + H_2O_2 = 2\ HI + O_2.$

Such explanations were only moderately successful in explaining the experimental results. The first major advance in describing a mechanism of hydrogen peroxide catalysis can be found in the classical work of Haber and Willstater (8) and Haber and Weiss (9), dealing with the homogeneous catalysis by iron ions in dilute aqueous solutions. To describe the decomposition by ferrous salts in acid and neutral solution the following cycle was proposed:-

$$Fe^{++} + H_2O_2 = Fe^{3+} + OH^- + OH \quad (1)$$

$$OH + H_2O_2 = H_2O + HO_2 \quad (2)$$

$$HO_2 + H_2O_2 = O_2 + H_2O + OH \quad (3)$$

$$OH + Fe^{++} = Fe^{3+} + OH^- \quad (4)$$

The novel feature of this cycle was the use of the radicals HO and $HO_2$ in a reaction scheme which permitted bimolecular steps more plausible than the simple oxidation processes represented above by stoicheometric equations. Another original suggestion incorporated in the scheme was the importance of electron transfer steps as represented by equations (1) and (4). Regarding the scheme as a chain

process (1) and (4) are initiation and termination reactions respectively whilst (2) and (3) are propagation steps.

An outstanding development was found in the confirmation of the production of OH radicals in the work of Baxendale, Evans and Park (10), who showed that in the course of the above process vinyl polymerisation could be initiated and OH detected in the polymer. Similar demonstrations were made by Dainton (11) for the decomposition initiated by light and ionising radiation.

Later, Barb, Baxendale, George and Hargrave (12) modified the original theory following further work on the system iron + $H_2O_2$ in solution. They concluded that the reaction producing oxygen was not that of $HO_2$ with $H_2O_2$ but $HO_2$ or $O_2^-$ with $Fe^{3+}$. In addition, after further and extended experiments, Weiss (13) has revised the original mechanism to include a reaction between $Fe^{++}$ and $HO_2$ as a chain-ending step.

Evans, Hush and Uri (14) increased the understanding of the postulated reaction steps by providing carefully considered thermodynamic data, based chiefly on experimental work of Baxendale, Evans and Uri (15) for reactions between metal ions and the radicals.

The results of these workers using kinetic and the thermodynamic arguments can be summarised for one typical catalytic process viz. the decomposition of dilute $H_2O_2$ in acid solution by ferric ions in the following scheme. The sequence of steps is due to the kinetic argument, the free energy changes are inserted to indicate the plausibility of the step.

$Fe^{3+} + H_2O_2 = HO_2 + Fe^{++} + H^+$ (5)

$\Delta G$ = 31K. cals/mol.

$Fe^{++} + H_2O_2 = HO + OH^- + Fe^{3+}$ (1)

$\Delta G$ = 20K. cals/mol.

$OH + H_2O_2 = HO_2 + H_2O$ (2)

$\Delta G$ = 19K. cals/mol.

$HO_2 = H^+ + O_2^-$ (6)

$\Delta G$ = 3K. cals/mol.

$Fe^{3+} + O_2^- = Fe^{++} + O_2$ (7)

$\Delta G$ = -34K. cals/mol.

$Fe^{++} + HO_2 = Fe^{3+} + HO_2^-$ (8)

$\Delta G$ -7K. cals/mol.

$Fe^{++} + HO = Fe^{3+} + HO^-$ (4)

$\Delta G$ = -19K cals/mol.

The working of this chain mechanism depends on the formation of a minute amount of $Fe^{++}$ in an electron transfer reaction (5). This then reacts in (1) forming hydroxyl radical which then produces perhydroxyl in (2). It may then replemish the $Fe^{++}$ concentration by reducing $Fe^{3+}$, (7), via the anion, $O_2^-$, of $HO_2$ which is fairly strong acid. The main features of the catalytic process are represented by the sequence of reactions (7), (1) and (2), the equilibrium (6) being assumed.

These principle features, derived to explain homogeneous catalysis, have been used by Weiss (16) to form the basis of a discussion of the heterogeneous decomposition of $H_2O_2$ solution on metal surfaces. The rate controlling and chain initiating step was again suggested as an electron

transfer to the $H_2O_2$ - the electron coming from the metal - with the formation of $OH^-$ and OH. The theory was tested by varying the electrical potential applied to a metal electrode immersed in $H_2O_2$ solution and observing the effect on the evolution of oxygen. It was found that the catalytic reaction was favoured by adjusting the potential so as to increase the availability of electrons at the metal surface. This electron transfer mechanism received added experimental support by the work of Dowden and Reynolds (17), who observed that with a range of Cu/Ni alloys, the copper rich mixtures were the best catalysts in neutral solution between 20 and 80°C. The rate of $H_2O_2$ decomposition was shown to increase with increasing copper content in accordance with a process controlled by the rate of transfer of an electron from the metal to the substrate.

Weiss (16) suggested also that the formation of a dissolved metal ion might result from the initial electron exchange between the metal and $H_2O_2$. This complication is always present in solution work and had previously been referred to by Wiegel (18) who showed that catalysis by finely divided silver was accompanied by solution of the metal until the product $C_{Ag^+}.C_{HO_2^-}$ had reached a steady value. Weiss interpreted Wiegel's results as follows:-

$$Ag \text{ (solid)} + H_2O_2 = Ag^+ \text{ (aq.)} + OH^- + OH \qquad (9)$$

$$Ag \text{ (solid)} + OH = Ag^+ \text{ (aq.)} + OH^- \qquad (10)$$

$$H_2O_2 = H^+ + HO_2^- \qquad (11)$$

$$Ag^+ \text{ (aq.)} + HO_2^- = Ag + HO_2 \qquad (12)$$

By applying the steady state principle, it may be shown that this cycle

leads to the conclusion that the product $C_{Ag^+} . C_{HO_2^-}$ must assume a steady value. Reactions (11) and (12) illustrate the importance of pH. High pH's favour catalytic decomposition of $H_2O_2$, and it is seen here that a high concentration of $HO_2$, which would occur at high pH values, should have this effect.

Broughton and Wentworth (19) studied the catalysis by $MnO_2$ and showed that $Mn^{++}$ accumulates in solution until the solubility product $C_{Mn^{++}} . C^2_{OH^-}$ is reached. They further asserted, on the basis of radioactive tracer experiments, that $Mn^{++}$ in solution is in a constant state of exchange with the manganese ions in the oxide surface. Broughton et al. (20) were not able to find evidence for such an effect with cobalt oxides; so in the absence of other support it is not possible to conclude that this exchange effect is general.

Recent work by Voltz and Weller (21) has been directed towards obtaining a correlation, for aqueous $H_2O_2$ decomposition, between catalytic activity and surface oxidation state. The catalysts used were chromia and chromia/alumina which had been pretreated at 500°C in an atmosphere of hydrogen or oxygen, and it was found that the oxidised catalysts were 6-8 times more active than the reduced ones. On the same theme, Mooi and Selwood (22) showed that manganese oxide catalysts supported on $Al_2O_3$ gave a peak activity in the decomposition reaction, which was shown by magnetic susceptibility measurements to occur at 3.6 Mn. They interpreted this peak as being due to a maximum induced oxidation state of the surface held manganese.

Schwab (23) examined the liquid phase decomposition of $H_2O_2$ by the spinels MgO. $Fe_2O_3$ and ZnO. $Fe_2O_3$, in order to assess the effect of replacement in this structure of $Mg^{++}$ by $Zn^{++}$. The pure magnesium ferrite was the better catalyst but a 10% replacement by Zn improved its efficiency to a peak 30% higher. In these investigations the authors (21, 22, 23) assumed that hydration and dissolution effects were unimportant. However, working in the liquid phase always entails a great deal of uncertainty in this aspect.

(b) Vapour Phase.

Hydrogen peroxide vapour, if not diluted too much by water vapour or other foreign gases, decomposes to water and oxygen with the characteristics of a flame as first demonstrated in the laboratory by Hart (24), and later studied in detail by Satterfield et al. (25).

The kinetics of this process have been difficult to study because of the intervention of the heterogeneously initiated decomposition. Recent work, however, in flow systems has been able to separate the two. Satterfield and Stein (26) showed that in glass vessels a heterogeneous process with energy of activation approximately 10K. cals/mol. (calculated assuming first order kinetics), was superseded above 500°C by a surface independant reaction with $E_A$ = 50-60K cals/mol. Stein's work offers support for the theory that $H_2O_2$ decomposition is initiated, here thermally, by splitting the oxygen - oxygen bond to give two OH radicals which would require 56K. cals/mol (14).

As stated above, there have been comparatively few previous investigations on the decomposition of hydrogen peroxide by solid

catalysts in the vapour phase. In 1923, Hauser (27) passed the vapour of 3% $H_2O_2$ over typical catalysts in the form of gauzes and found that copper and iron destroyed little while asbestos destroyed most of the $H_2O_2$. Such an observation could, of course, have little relevance to the chemical nature of the catalyst since the surface areas were very different and not measured. In the same year, Hinshelwood and Pritchard (28) made a brief kinetic study of the decomposition in glass bulbs at 76°C and found the reaction to be heterogeneous and of the first order in $H_2O_2$ concentration.

Later, Elder and Rideal (29) made a more detailed study of the decomposition on quartz, glass and platinum wire in the temperature range 80-100°C, using 60% $H_2O_2$ vapour. The kinetics were found to be first order on the platimum and glass surfaces, but on quartz zero order was indicated and the decomposition came to an end at 15% completion. The quartz results were criticised by Rosenberg and Kistiakowsky (30) who found poor reproducibility in quartz vessels at 85-90°C, but the reaction always went to completion.

Reuter and Gaukham (31) set out to compare the decomposition on the same catalyst in the liquid and vapour phases. For the vapour phase work they distilled 30% $H_2O_2$ over a catalyst consisting of smooth or platinized platinum, or manganese or lead dioxide. They concluded that the mechanism of the vapour phase decomposition was essentially similar to that in solution. The reaction was found to be first order in both cases, but the results published do not exclude the possibility of diffusion of $H_2O_2$ to the catalyst surface as being the common rate controlling factor.

Mackenzie and Ritchie (32) made a much more accurate and detailed study of the system with quartz at pressures varying from 0.6 - 1.2 mm Hg. The procedure involved introduction of hydrogen peroxide by vaporisation from a quantity of highly concentrated liquid and the rate of reaction was followed by the pressure change. They found the reaction to be second order with respect to $H_2O_2$ in the temperature range 15-150°C. (This is the only case where second order dependance was observed. As reported later, similar results were found in a static system during the present investigation, which are differently interpreted).

Again in static systems Baker and Ouellet (33) and Giguère (34), carried out a wide series of investigations using different forms of glass and quartz, and with vessels coated with tin and aluminium. The reaction was generally first order in the range of conditions used, (80-200°C and 50-100 mm. Hg pressure); and for the glass surfaces apparent energies of activation of 13.4-19K. cals/mol. were calculated from the velocity constants at different temperatures. Soft glass was the most active catalyst with pyrex, tin and aluminium next in descending order of activity. Quartz, which at low temperatures gave a marked period of induction before any decomposition was observed, was the least catalytic surface. However, Giguère's work lends itself to the critiscism that hot chromic acid was used as the cleaning agent which would probably leave chromium oxides on the glass surface. This otherwise very accurate series of experiments must be considered to be fallible on this point.

McLane (35) has studied the decomposition on pyrex glass with and without a coating of boric acid, in the temperature region 470-540°C in

a flow system with $H_2O_2$ partial pressures 1-2 mm. Hg. The reaction rate was found to obey a first order relation, and was somewhat slower in the coated vessels. The inhibitor action may be due to the conversion of the basic oxides in the glass surface to inactive borates. Harris (36) made a brief study of the decomposition on a quartz reaction tube by bubbling nitrogen at one atmosphere through 65% aqueous $H_2O_2$ held at 52°C. He found that the decomposition rate was increased by coating the tube with potassium chloride, and reported a half life of 0.5 secs. at 520°C in a clean vessel.

Very recently, Giguère and Liu (37) have measured the rate of decomposition of $H_2O_2$ vapour by a static method, at pressures between 0.2 and 20 mm Hg in the temperature range 300-600°C, using glass vessels. The reaction was found to be first order, with an activation energy of 10-12K cals/mol below 400°C and 48K cals/mol above this temperature, which these authors take as the transition point from the heterogeneous to the homogeneous decomposition process. In this instance the cleaning procedure adopted was to treat the vessels with hot fuming sulphuric acid followed by hot concentrated hydrogen peroxide, which would seem to be a more satisfactory method than that employed in the earlier work (34).

It will be evident from the above account that the vapour phase work has not progressed far towards yielding a clear picture of the mechanism of the catalytic reaction. No detailed study of the surfaces normally considered to be most active, such as silver or manganese dioxide, has been made. In addition, no conclusions have been drawn as to the connection between the chemical nature of a catalyst and its activity.

However, in the case of the work at low pressures, first order dependance on hydrogen peroxide concentration is usually found which suggests that the rate controlling step could be either (a) gas phase diffusion of $H_2O_2$, (b) diffusion through a layer of water vapour held at the surface or (c) adsorption of $H_2O_2$.

In all these processes the rate of decomposition would depend on the first power of the hydrogen peroxide partial pressure. Diffusion seems to be ruled out by the high and variable energies of activation found by Giguère (34) and also by the sensitivity of the catalytic activity to minor changes in the treatment of surfaces. It may then be concluded that in the majority of the experiments reported, adsorption is probably the rate-controlling process.

(2) Catalysis and Surface Composition

Whether or not adsorption is the kinetic rate controlling step in a particular catalytic process, it is the unique step without which the reaction is not possible. Furthermore it is equally evident that it is chemisorption which is relevant since by definition this is the type of adsorption which involves the chemical bonding of the adsorbed species. (This is not to say that in a given process van der Waals adsorption may not be important as for example by maintaining a loose surface layer of reactants, products or intermediates).

The question which arises is what kind of surface feature will be relevant to the chemisorption of an $H_2O_2$ molecule. We may approach this by considering what type of chemical bond weakening would lead to the decomposition of $H_2O_2$.

As we have mentioned, thermal decomposition in the vapour phase (McLane (35) and Satterfield and Stein (26) ) seems to be associated with rupturing of the O-O bond, while light is held to act similarly (see Dainton (11) ) and solution phase homogeneously catalysed decomposition mechanisms involve breaking of the O-O bond in an $H_2O_2$ molecule after acceptance of an electron. Thus it is natural to consider as a first possible surface process.

$$H_2O_2 + 2S = 2SOH$$

Where S represents a surface site and SOH an OH radical adsorbed on such a site. Since an $H_2O_2$ molecule which has accepted an extra electron is in an unstable state with regard to the O-O bond, (the extra electron goes into an antibonding orbital and reduces the net bonding between the oxygen to zero), it is attractive to consider that the most likely precursive step to catalysis is

$$H_2O_2 + 2S = 2S^{+} - H_2O_2^{-}$$
$$= 2S^{+\frac{1}{2}} \ldots OH^{-\frac{1}{2}}$$

in which the final product can be thought of as a "loose" hydroxide - which may in suitable conditions become normal hydroxide or react further to give water and oxygen. Consideration of this mechanism may be left until later but it would not be inappropriate at this stage to consider the properties of oxides which may help to an understanding of the possible nature of S.

The oxide surface is, of course, a complex system. In addition to surface metal ions, $M^{+}$, $M^{++}$ etc. and oxide ions $O^{=}$, there will be surface ionic defects of either kind (anionic or cationic) with associated electronic irregularities. There will also be, on an oxide prepared normally, adsorbed impurities such as excess oxygen or water. We shall also have to consider the

possibility of trace impurities.

(a) Defect Structure of Oxides.

In the past fifteen to twenty years a new conception of solid state physics has arisen through the postulation of defect structures to explain many chemical and physical properties of solids. The theory of these phenomena has been described in the classical work of Mott and Gurney (38), and extensive experimental and theoretical investigations have been completed by many workers which has been integrated into a treatise on the existing conception of solids by Shockley (39).

In a stoichimetric crystalline compound displacement of atoms from their regular lattice sites may occur. The resulting interstitial atoms and vacant lattice sites are distributed at random through the crystal. Two simple limiting cases of defect formation are possible:-

(1) Equal concentrations of vacant cation and vacant anion sites (Schottky defects).

(2) Interstitial cations or anions with a corresponding number of vacant lattice sites (Frenkel defects).

Cases (1) and (2) may be considered to be inherent thermal defects, which at normal temperatures are few in comparison to many other deviations from stoichiometry which have come to be recognised. For example, in the case of metal oxides, excess metal may be incorporated by converting some cations effectively into neutral atoms or into cations of lower valency, whilst the accomodation of excess oxygen involves the presence of cations of higher valency. Each atom of excess metal represents an extra cation plus a trapped electron in the lattice and

constitutes a filled impurity level from which, by fluctuations of thermal energy, the electron may be excited to the conduction band of the oxide. A cation of higher valency, in an oxide with excess oxygen, is a site of electron deficiency; an empty impurity level to which an electron may be excited from the originally filled valency band of the crystal. Electrons in the first case, and positive holes (valency electron vacancies) in the second case are thereby rendered mobile, giving rise to electronic conductivity. On this basis metallic oxides may be classified according to their electronic (semi-conducting) characteristics.

Cuprous oxide is an example of a "p-type" semi-conductor in which the electronic conductivity is due to positive holes arising from oxygen excess or metal deficiency. The electrical neutrality of the crystal is preserved by the existence of an equal number of cupric ions and vacant cuprous cation sites in the lattice, as follows:-

$Cu^{+}\oplus$ $Cu^{+}$ $\square$ $Cu^{+}$

$O^{=}$ $O^{=}$ $O^{=}$ $O^{=}$

$Cu^{+}$ $Cu^{+}\oplus$ $Cu^{+}$ $\square$

Where $\oplus$ = positive hole

and $\square$ = vacant $Cu^{+}$ site.

p-type oxides exhibit a tendency for the metal to pass to a higher valency state by adsorption of oxygen. The positive hole produced in the electron transfer diffuses into the lattice to some extent, whilst the adsorbed oxygen may be built into the surface (41).

This process has been studied very fully for $Cu_2O$ by Garner and his coworkers (44, 46, 47) whose results, among other things, demonstrated a marked rise in conductivity when oxygen was adsorbed by $Cu_2O$. This could be explained by a creation of electron defects thus

$$Cu^{+} + O_2 = Cu^{+}\oplus + O_2^{-}$$

where $Cu^{+}$ is here a surface ion and the $O_2^{-}$ is an unstable adsorbed molecule. The above workers preferred to consider that oxygen is rapidly dissociated to form $O^{-}$ or even $O^{=}$ although the latter ion is a special adsorbed species and not ordinary lattice oxygen until metal ion diffusion has taken place to capture it. $Cu^{+}\oplus$ is a p-hole and is responsible for electronic conduction.

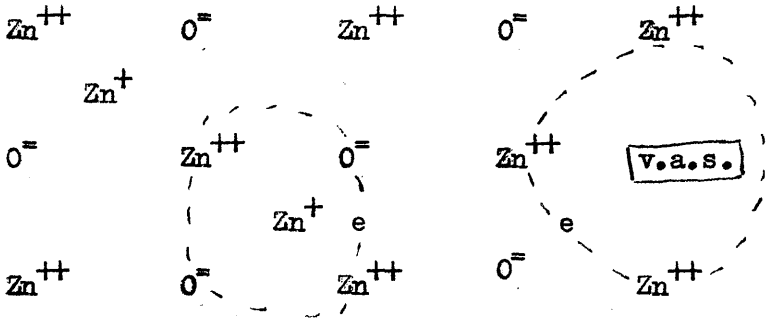
At low temperatures the lattice defects will diffuse negligibly slowly but the electrons (or p-holes) will remain mobile. The temperature at which ionic defects become mobile is around $100^{\circ}C$ for $Cu_2O$ surfaces. It may be judged from the temperature at which the oxide film on a metal is no longer fully protective and begins to grow slowly.

In a normal, or n-type, semi-conducting oxide the electronic conductivity is due to the movement within the crystal of free electrons or excess electrons which may arise from loss of oxygen or the inclusion of slight excess of metal atoms which then dissociate:-

$$M = M^{+} + e$$

Typical examples are ZnO or CdO. The excess metal atom is probably to be considered as in an interstitial lattice position. The electron will normally be attached either to a normal $M^{++}$ lattice ion from which it can escape freely with only thermal energy, an interstitial ion, or in the

neighbourhood of missing oxygen ions (vacant anion sites) which will be particularly abundant at the surface of the oxide crystal. For ZnO we could have:-




Where e = quasi-free electron

$Zn^+$ = interstitial zinc ion (There is, at the moment, no conclusive evidence to show whether this zinc is present as atoms or ions. Wagner (42) suggests the ion $Zn^{++}$ Gray (43), $Zn^+$).

These n-type semi-conducting oxides have a tendency to lose oxygen with the formation of interstitial metal ions, and quasi-free electrons which act as the current carriers.

A third type of oxide comprises the highly refractory ones like $Al_2O_3$ and MgO. These oxides are insulators, being quite non-conducting at normal temperatures but on heating in vacuo at 1000°C they can lose oxygen and become similar to the n-type semi-conductors.

For the purpose of this investigation the tendency, inherent in its properties as a semi-conductor, of the oxide to hold oxygen as $O_2^-$ or $O^-$ in an adsorbed condition will be considered to be an important criterion in the catalysis of $H_2O_2$.

(b) Oxide film growth on metals.

As a source of evidence for the surface structure of oxides we

must consider the work on the growth of oxides on metals. The practical work has been kinetic and calorimetric and provides a complex field of data. Basically, however, one general mechanism is sufficient to explain the results. Oxygen is adsorbed at the surface of the oxide film and being strongly electronegative it attracts as electron from the oxide. An electron comes from the underlying metal to neutralise the positive charge caused in the oxide surface and in so doing gives rise to a cation at the metal/oxide interface. Electrons are transported either as electrons or p-holes. Metal cations must also be transported across the film.

(c) Catalytic Reactions on Solid Oxides.

Through the application of these new ideas of the solid state, novel interpretations have been advanced to explain the role of a catalyst in a heterogeneous reaction. Although a fundamental understanding has not yet been completely attained; there is little doubt that any interpretation of the activity of an oxide catalyst in some reactions must take close account of its properties as a defect solid.

An extensive contribution in the field of gas/solid reactions has been made by Garner, Stone, Gray and co-workers at Bristol. They have succeeded in establishing a correlation between catalytic activity and electronic structure of certain metal oxides for the $CO/O_2$ reaction (44) and the decomposition of $N_2O$ (45). For the $CO/O_2$ reaction Garner, Gray and Stone (46, 47) proposed a reaction mechanism for the more reactive catalysts, especially $Cu_2O$. They regarded the chemisorption of oxygen on cuprous oxide as involving the process:-

$$O_2 + 2e = O^- + O^- \qquad (1)$$

Wagner and Hauffe, (48) had already suggested the initial step:-

$$N_2O + e = O^- \text{ (ads.)} + N_2 \qquad (2)$$

to explain the catalysis of $N_2O$ by NiO at 500 - 600°C. These workers observed that the electronic conductivity of the nickel oxide was enhanced during catalysis. Since it was known that electrical conductivity of these p-type oxides was due to an electron deficiency, it was reasonable to assume that it would be increased during the occurrence of reaction (1). Gray (49) and Gray and Savage (50) used conductivity measurements to follow the adsorption and desorption of oxygen by the oxide which, on the mechanism indicated by equation (1), would also be accompanied by changes in the number of electron defects in the oxide. The second stage in the catalysis of $N_2O$ decomposition begun as in equation (2), is

$$2O^- \text{ (ads.)} = O_2 + 2e \qquad (3)$$

or

$$O^- \text{ (ads.)} + N_2O = O_2 + N_2 + e \qquad (4)$$

and since Gray and Savage showed that the desorption of oxygen from $Cu_2O$ was a very slow process it may be inferred that reactions (3) and (4) are probably rate controlling. This point has been substantiated by Hauffe, Glang and Engell (51) who studied that decomposition of $N_2O$ on a variety of oxides including NiO. They found that the catalytic activity of the oxide was improved by the addition of small traces of $Li_2O$, which increased the p-type character, and thus would accelerate the desorption rate through the creation of positive holes able to consume electrons.

Garner, Stone and Tiley (44) and Dell and Stone (52) examined the $CO/O_2$ reaction on $Cu_2O$ and NiO films present as a layer on the metal. They concluded that an important part of the scheme was the reaction of adsorbed oxygen and adsorbed carbon monoxide to give an adsorbed

$-CO_3^=$ complex.

$$CO + 2O^- = CO_3^= \qquad (5)$$

This was reversible below 100°C since the CO could be removed by evacuation, but above 100°C it reacted to $CO_2$. In the presence of excess CO the complex reacts:-

$$CO_3^=(ads.) + CO = 2CO_2\ (g) + 2e \qquad (6)$$

The slowest step in the $CO/O_2$ catalysis according to these investigators was the adsorption of oxygen. The very slow desorption of oxygen was not involved. This would explain why $Cu_2O$ was active at lower temperatures (0-100°C) than for the $N_2O$ decomposition (200-250°C) which can only proceed by the direct desorption of oxygen.

The catalytic oxidation of CO on NiO has also been studied by Parravano (53) who suggested that at low temperatures (100-180°C) the rate controlling process was the adsorption of oxygen, whilst between 180-240°C the slow step was the removal of surface oxygen by carbon monoxide to give $CO_2$. In addition, the system NiO + foreign ions was investigated (54) in order to ascertain how the catalytic activity would be affected by modifying the oxide electronic type. In the low temperature range all the catalysts gave the same value for the activation energy, but at the higher temperatures it was found that monovalent cations increased whilst trivalent decreased the activation energy of the reaction. These findings are in apparent contradiction to those of Schwab and Block (55) who report that an increase in p-type character lowers the activation energy in the temperature range 250-400°C to 12K.cals/mol, whilst a decrease of p-type character by

adding $Cr^{3+}$, raised the activation energy from 14 to 19K. cals/mol.

Stone (56) has tried to reconcile these findings by suggesting that the rate controlling step is, in each case, at a different stage in the reaction cycle. However, it may be possible that the lack of catalyst specificity found by Parravano at low temperatures is due to the reaction being partly subjected to transport control, which disappears as the temperature is raised. In addition, as has been pointed out by Verwey (57), when preparing an impurity type semi-conductor the foreign ion should be about the same size as the ion for which it is substituted. This will preserve the original lattice without distortion or dislocation. By adding $Cr^{3+}$ and $Li^{+}$ as trace impurities, Schwab and Block would not appreciably alter the NiO lattice. On the other hand, Parravano used $Ag^{+}$ as an additive which has twice the ionic radius of $Ni^{++}$, and this may have caused lattice collapse, resulting in a non-homogeneous structure saturated with defects. If this were so, then the catalysts used in the two series of experiments are not strictly comparable.

This impurity addition method of preparing catalysts of varying defect properties has also been applied to the decomposition of $N_2O$ by Wagner (58) and to the Hydrogen/Deuterium exchange reaction by Molinari and Parravano (59) and Heckelsberg et al. (60). In these cases variations in quasi-free electron concentration in ZnO were accomplished by suitable additions of $Li^{+}$, $Al^{3+}$ or $Ga^{3+}$. Measurements made by Parravano (61) on the reduction of nickel oxide by hydrogen, have shown a greater activation energy with increasing p-type character of the oxide by the addition of small amounts of $Li_2O$, $Ag_2O$ etc. By the inclusion of these impurities it is possible to obtain a semi-conductor in which some

of the metal ions have been brought into a higher valency state, p-type, or one in which they have a tendency to pass into a lower valency state, n-type.

Finally, the recent work of Gray and Darby (62) on the $H_2/O_2$ reaction should be mentioned, as it is of interest from the mechanistic point of view. The reaction was studied in the temperature range -21°C to 137°C on an evaporated nickel film, surface oxidised. An activation energy of 3.4 K.cals/mol was determined and the rate was dependant on the square root of the oxygen concentration. The availability of $Ni^{++}$ ions was suggested as being the most important rate determining factor; the adsorption mechanism being suggested as :-

$$O_2 + 2\,Ni^{++} \rightleftharpoons 2O^- + 2\,Ni^{2+}\oplus \qquad (a)$$

$$2O^- + 2\,Ni^{++} \rightleftharpoons 2O^= + 2\,Ni^{2+}\oplus \qquad (b)$$

and for the desorption the reverse process was held to occur.

(d) Physical properties of oxide catalysts.

It is well known that oxide catalysis is very susceptible to the conditions of pretreatment of the oxide. Among the physical properties which have been used to characterise a given preparation are specific surface area, electrical conductivity and Hall effect, crystal structure and magnetic susceptibility.

The latter property seemed particularly relevant to many of our oxides which were based on transition elements with several possible valencies.

(i) Magnetic susceptibility and catalysis.

Hüttig (65, 66) studied the decomposition of methyl alcohol on the

$ZnO/Cr_2O_3$ catalyst system. He found that the catalytic activity of the mixture varied with the temperature of heat treatment, and these variations were closely accompanied by changes in the magnetic susceptibility of the mixtures. For the equi-molar mixture the activity reached a sharp maximum at 400°C, a steep rise in susceptibility with incipient ferromognetism being observed also at this temperature. These results were critisised by Selwood (67) who suggested that paramagnetic impurities may have been present in the mixtures and, to make an adequate distinction, the magnetic susceptibility measurements should have been determined at different temperatures.

Selwood (67, 68) has reviewed the various techniques available for making susceptibility measurements, and has stressed the importance of making determinations at two or more field strengths, since although paramagnetism is independant of field, minute traces of ferromagnetic impurities can be detected in this manner. A graph of susceptibility against reciprocal field strength will yield the true susceptibility of the sample by extrapolating to infinite field. In addition, it has been pointed out that paramagnetism frequently varies inversely with the absolute temperature, and by carrying out determinations at a series of temperatures the presence of paramagnetic impurities in a given sample can often be easily detected.

This susceptibility isotherm method has been applied by Selwood and co-workers to study the magnetic properties of supported oxides of manganese (69), and to the copper/chromium oxide spinel system (70). The onset of spinel formation found at 1000°C for $CuO.Cr_2O_3$ has been

disputed by Stroupe (71) who reports X-ray measurements in favour of his contention. It is possible that Selwood's active catalyst was a solid solution of the two oxides, or merely $Cr_2O_3$ supported on CuO, but from the point of view of catalyst activity it should be stressed that the type of structure is unimportant, rather that structural changes can be related to catalytic activity.

Hüttig and his collaborators investigated the catalytic activities of mixed oxides of the composition $XO/Y_2O_3$, and related this to various physical properties, in addition to susceptibility, such as crystal structure and powder density etc. (72, 73). Spinel formation was found to occur around 800°C for most of the systems investigated and coincided with loss of catalytic activity. It was concluded that although the final spinel state was not so effective in catalysis, the various stages in the transition from a mechanical mixture to this structure were of primary importance.

(ii) (b) Surface area and catalysis.

The major contribution in this field came from the classical work of Brunauer, Emmett and Teller (74), and Emmett and Brunauer (75) on multilayer physical adsorption. The method used by these authors was successful in measuring areas of not less than one square metre, generally by nitrogen adsorption at liquid air temperatures. Later, by using ethylene at - 195°C as the adsorbate, Duncan (76) and Wooten and Callaway - Brown (77) were able to extend the method to measure areas in the region of 100 sq. cms. This treatment, although not yielding absolute values of surface area, is the best at present available. It suffers from the defect that when the pores in a solid are sufficiently close to molecular

dimensions, the smaller capillaries cannot be reached by the adsorbate molecules, and is thus not applicable to surfaces having a roughness factor close to unity.

Since these methods are based on physical adsorption they offer no means of determining the number of "active sites" on a catalyst surface. Nor indeed are they any indication of the variety of adsorption sites which may be available on a given catalyst.

Early conceptions, which regarded a catalyst as having a fixed surface with a variety of specially active "free valencies" (Taylor, 78) due to the position of the ions being on edges or peaks of surface crystallites, have to be modified in the light of the work of Volkenshtein (79), who emphasised the defect nature of a surface and drew particular attention to the equilibrium which could be assumed to exist between various types of ionic and electronic defects. In such cases a chemisorbed molecule is an impurity in the surface and gives rise to shifts in the surface equilibrium. Thus a surface with chemisorbed molecules attached has different properties from the same solid before the attachment.

Boudart (80) has extended this view by concluding that active centres in a surface will be mobile and will be in a process of continual creation and destruction. Naturally enough ionic defects and equilibria involving them will not be mobile at the lower temperatures and will only be slightly so for most oxides at the higher temperatures which we used in our investigations (180°C).

(3) The Present Approach

Hart and McFadyen (81) investigated, in considerable detail, the vapour phase decomposition of hydrogen peroxide on cuprous oxide films supported on copper

metal. This was used in the form of a gauze held normal to a flowing stream of gas containing $H_2O_2$ vapour. They also made a few measurements on other oxidised metals available as gauzes e.g. Fe, Ag and Pt. They worked with partial pressures of $H_2O_2$ in the region of 1 mm. and in a temperature range of 40 - 100°C. The activation energy of the reaction on the $Cu_2O$ covered gauzes was determined as being about 15K. cals/mol and the kinetics were first order with respect to $H_2O_2$ concentration.

The temperature coefficient of the reaction rate was found to vary with the "previous history" of the catalyst. This effect has been discovered by many investigators in the field of heterogeneous catalysis, including Constable who observed variations in activation energy between 18-24K cals/mol. for the dehydrogenation of ethyl alcohol also on cuprous oxide (82).

The extensive results of Hart and McFadyen on the $H_2O_2/Cu_2O$ catalysed reaction, led them to conclude that the property of the oxide which determined its catalytic efficiency was related to its ability to adsorb oxygen, somewhat analogous to the findings of Dell, Stone and Tiley (45) on the $N_2O$ decomposition and the catalysis of the $CO/O_2$ reaction on cuprous oxide.

The initial aim of the present work was to extend the work of Hart and McFadyen to a wide range of metal oxides of different types, so as to enable a correlation to be made between the properties of an oxide and its catalytic efficiency. It was realised that this would involve the development of a method suitable for the use of bulk oxides rather than oxidised metal gauzes, so that carefully prepared pure oxides of known bulk properties could be used. However, an important object was to maintain a link with the earlier work, and therefore in some cases a careful study was made of the catalysis achieved by different forms of a given oxide - oxidised metal slip, fully

oxidised flashed metal film on glass, and finally, compressed bulk oxide slip.

Arising out of this it was essential to give attention to the methods of preparation, particularly the thermal pre-treatment, of oxides and its relevance to catalytic efficiency.

The second aim was to study how to modify the catalysis by a given oxide, through the addition of foreign oxides in either trace or equi-molar amounts. The object of this was to link catalysis with solid oxide properties which are known to be affected by such inclusions. For example, the intention was to study NiO with additions of $Li_2O$ and $Ga_2O_3$. The former is known to increase, and the latter to decrease, the tendency of the oxide to hold adsorbed oxygen at its surface.

For the equimolar mixture studies, CuO and $Mn_2O_3$ were chosen with equi-molar amounts of a range of other oxides, e.g. $Fe_2O_3$, ZnO, NiO, $Al_2O_3$.

The full identification of what has been referred to above as "efficiency" of a catalyst is a difficult matter. The intention in this work was to measure the fraction of $H_2O_2$. decomposed under constant flow conditions and to support this with measurements of temperature coefficients. In addition, as a possible source of comparative data on different oxide catalysts, the surface areas of some of the slips would be measured by a B.E.T. gas adsorption method.

Paramagnetic measurements were also planned as a possible source of information about the nature of the metal ions in mixed oxides, and X-ray structural analysis to give an indication of compound formation in such mixtures during heat treatment.

Finally, as an indication of the relation between the flow studies and

the previous work using static methods, it was intended to carry out a brief study in a static apparatus of one or more suitable catalysts.

EXPERIMENTAL

(1) Apparatus and Method.

(a) Flow system. General description.

A flow method for examination of the catalysts was chosen in order to disclose changes of catalytic efficiency with time, and to be able to treat these changes separately from the normal kinetics which assume a constant catalyst. In addition, practical advantage of such a system was that it would be possible, by suitable choice of flow arrangements, to eliminate gas phase diffusion of the hydrogen peroxide to the catalyst surface as a possible rate controlling factor.

A method in which the vapour of pure or very concentrated hydrogen peroxide was pumped over the catalyst at reduced pressure presented the main difficulty that the catalyst temperature during the decomposition process would rise well above that of the vapour stream. This could be avoided by using vapour from solutions of low concentration hydrogen peroxide, which would however, involve having always a large amount of water vapour present as a diluent in the gas stream. It seemed preferable to work with an inert carrier gas such as nitrogen, at atmospheric pressure. The partial pressure of the $H_2O_2$ could be kept low enough to limit the temperature rise on the catalyst to 1 or 2 degrees. Working at atmospheric pressure would permit easy precision regulation of the flow rate before the gas was passed through a saturator containing hydrogen peroxide solution at a controlled temperature.

The apparatus eventually used is shown in Fig. 1., up to and including the pre-heater, and was a modified version of that used by

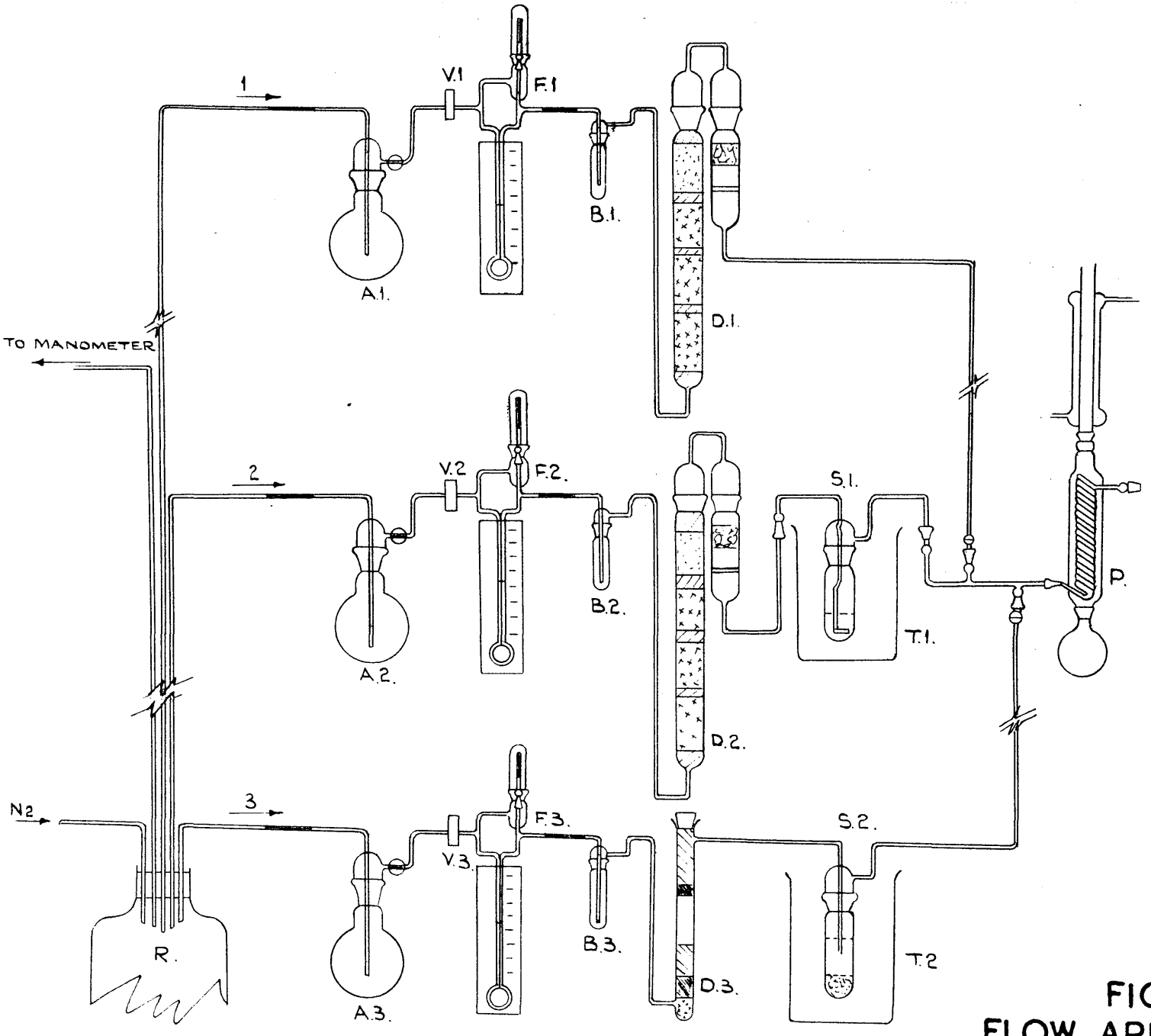



FIG. 1.
FLOW APPARATUS
LEGEND :- SEE TEXT

Hart and McFadyen (81).

"White-Spot" nitrogen (>99.99% nitrogen, British Oxygen Company), was drawn from a cylinder equipped with pressure gauzes and needle valves to adjust the rate of flow. This passed to a ten litre stock bottle (R) which acted as a storage vessel for the nitrogen, and also served to reduce to a minimum slight pressure fluctuations caused by the manostat (M) and the gas absorbers, not shown in diagram. Fine control of flow was obtained by carefully manipulating the cylinder needle valves to give a pressure of 125 $\pm$ 0.5 mms. Hg above atmospheric in the system, which was kept at this constant value by the manostat.

The manostat is shown in Fig. 2. It operated from a simple Hg filled U - tube manometer with a capillary inserted to prevent the mercury see-sawing. With rising pressure in the storage bottle electrical contact was made in one arm, as in a thermostat bath regulator. Through a relay, this caused a leak-off to be opened. The leak-off consisted of a capillary closed by a 100 gm. steel weight with soft rubber attached to the underside, which pressed against the ground end of the capillary. A solenoid, fixed above this weight, was able to raise it when energised. The relay operated on a difference of pressure of less than 0.1 mm Hg and kept the pressure in the nitrogen reservoir to within 0.2 mm of water.

From the reservoir (R) the nitrogen could be drawn off into any one of three streams as indicated in the diagram, viz:-

(1) Diluent nitrogen to adjust the concentration of vapour entering the reaction tube in determining the reaction order, and to "dry out" the apparatus, especially the reaction-tube, after cleaning.

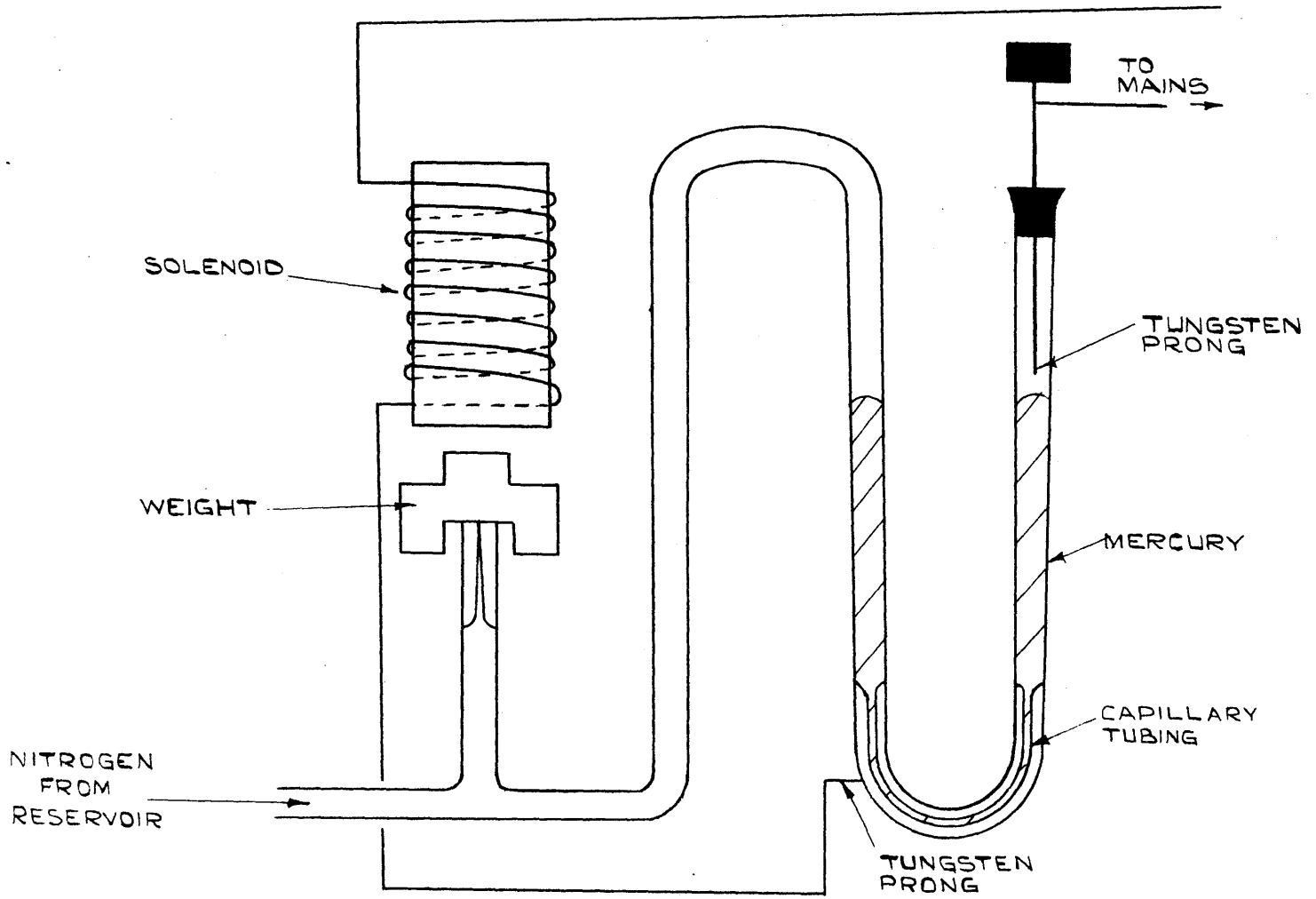



FIG 2.
MANOSTAT ASSEMBLY

(2) The saturator stream in which nitrogen was bubbled through liquid hydrogen peroxide held at a constant temperature.

(3) The water vapour stream in which the nitrogen was passed through a saturated solution of magnesium chloride held at a constant temperature which enabled a known amount of water vapour to be added to the total gas flow.

Each stream could be operated independantly, or in conjunction with one or both of the others. This was accomplished by suitable manipulation of stopcocks and screw clips controlling the gas flow from the nitrogen reservoir.

The individual components in the flow system are detailed as follows:-

$(A_1)$, $(A_2)$, $(A_3)$. One litre B34 round-bottom flasks used as secondary nitrogen storage vessels to reduce pressure fluctuations to an absolute minimum. They were connected to the reservoir via capillary tubing which helped to insulate the flow systems from the large storage vessel.

$(V_1)$, $(V_2)$, $(V_3)$. Fine adjustment needle-valves. These gave fine control of the flow rate having a sensitivity of 2 mls/min. per degree of dial revolution at normal temperature and pressure.

$(V_3)$ was later replaced by an Edwards needle-valve to give an even finer degree of control, namely 0.5 mls/min. per degree of dial revolution, which was required in adjusting the flow from the water saturator in some of the later experiments.

$(F_1)$, $(F_2)$, $(F_3)$. Differential pressure type flow-meters as described by Farkas and Melville (83). The meters were constructed in pyrex glass with limbs 30 cm. long, internal diameter = 0.5 cm. The flow capillary

was connected to the exit limb of the meter by an A7 joint. Each flow-meter was securely bolted to a baseboard and scale from which the pressure differential was easily determined. The capillaries used were 0.6 mm. in diameter and of various lengths from 5-15 cm. depending on the range of flow-rates required, and could be easily interchanged by removing the quickfit spring and breaking the B19 joint which was lubricated by a vacuum grease.

The capillaries were calibrated directly by a moving soap film technique. This was a simple and accurate method in which the exit nitrogen from the flow-meter was passed just under the surface of a "soap" solution, consisting of 40% "Teepol", 30% glycerol and 30% water. This resulted in the formation of a thin film which moved along a glass tube, one metre long by 3 cm. internal diameter, with the gas flow. In order to prevent the film from bursting prematurely whilst moving along the calibration tube, considerable attention was paid to the cleanliness and freedom from grease of the tube surface, which was washed with distilled water and dried with acetone. The time of travel between selected fixed points was noted. By choosing suitable nitrogen pressures a graph was drawn of flow rate against pressure differential on the flow-meter water manometer. The volume of the tube between the points was determined by filling it with mercury and weighing.

Alternatively, calibration was accomplished by connecting a flow-meter in series with another of pre-determined characteristics. By these methods it was possible to gauge accurately to within 0.5%, rates of flow from 25-500 mls/minute which were required in the experiments.

The gas from the flow-meters passed through a further capillary to

prevent the flow-meter registering minute pressure fluctuations from the absorber/bubblers.

($B_1$), ($B_2$), ($B_3$). These were identical splash traps which prevented water from discharging into the apparatus in the event of a flow-meter being accidently overloaded.

($D_1$), ($D_2$). Identical cleaning towers, 60 cms. long by 4 cms diameter, to remove all dust particles or water vapour carried over in the nitrogen stream. The packing consisted of equal layers of filtering and drying materials arranged as follows:-

(a) glass wool, (b) calcium chloride, (c) glass wool,

(d) calcium chloride, (e) glass wool, (f) magnesium perchlorate and

(g) glass wool.

($D_1$) and ($D_2$) were connected in series to shorter towers, 30 cm. x 4 cm. i.d., containing cotton wool and a G4 sintered glass disc which was used to prevent any cotton wool fragments from being blown over in the inert gas stream.

($D_3$) A cleaning tower filled as for ($D_1$) and ($D_2$) but of smaller dimensions being 50 cm. long and 2 cm. internal diameter.

($S_1$) The hydrogen peroxide saturator, consisting of a pyrex tube 15 cm. long x 4 cm. id., the open end terminating in a B34 cone. The nitrogen supply entered through a 5 mm. bore tube which passed through a B34 socket forming the head of the saturator; and was discharged into pure or very concentrated hydrogen peroxide solution through a G1 sinter, which effectively distributed the inert gas as tiny bubbles through the body of the peroxide. The sinter was placed about 2 cm. from the bottom of the saturator, which contained 20 mls. $H_2O_2$.

The saturator was immersed in a 3 litre, stirred, thermostat bath. The temperature control was operated by an electronic relay which enabled the temperature to be held to $\pm$ 0.01°C. The bath was maintained at a temperature below that of the room (12-18°C, as chosen) to prevent condensation of the saturated vapour elsewhere in the system. The bath was continuously fed from the cold mains water supply and the volume kept steady by a constant level device. If the mains water temperature was too high, iced water from a gravity feed was added at rated of 50-110 mls/minute depending on the temperature required.

($S_2$) The water saturator, a pyrex tube 20 cm. long by 24 mm. i.d., the open end being a B24 cone; which contained a saturated solution of magnesium chloride. The nitrogen in stream (3) entered the B24 socket, which formed the head of the saturator, through a 5 mm. bore tube which tapered to a 2 mm. orifice at a distance of 2 cm. from the magnesium chloride crystals.

The saturator was immersed in a water bath, similar to that used for the $H_2O_2$ saturator described under ($S_1$). Care was taken not to exceed the saturated water vapour pressure under the prevailing atmospheric conditions when adjusting this temperature, - which was not, however, necessarily below room.

All ground joints in the apparatus up to this point, with the exception of the B34 joint in the peroxide saturator, were lubricated with either "Silicone" or "Apiezon M" grease. The joints following, i.e. those which came into contact with the hydrogen peroxide vapour, were not greased; in order to prevent contamination and possible

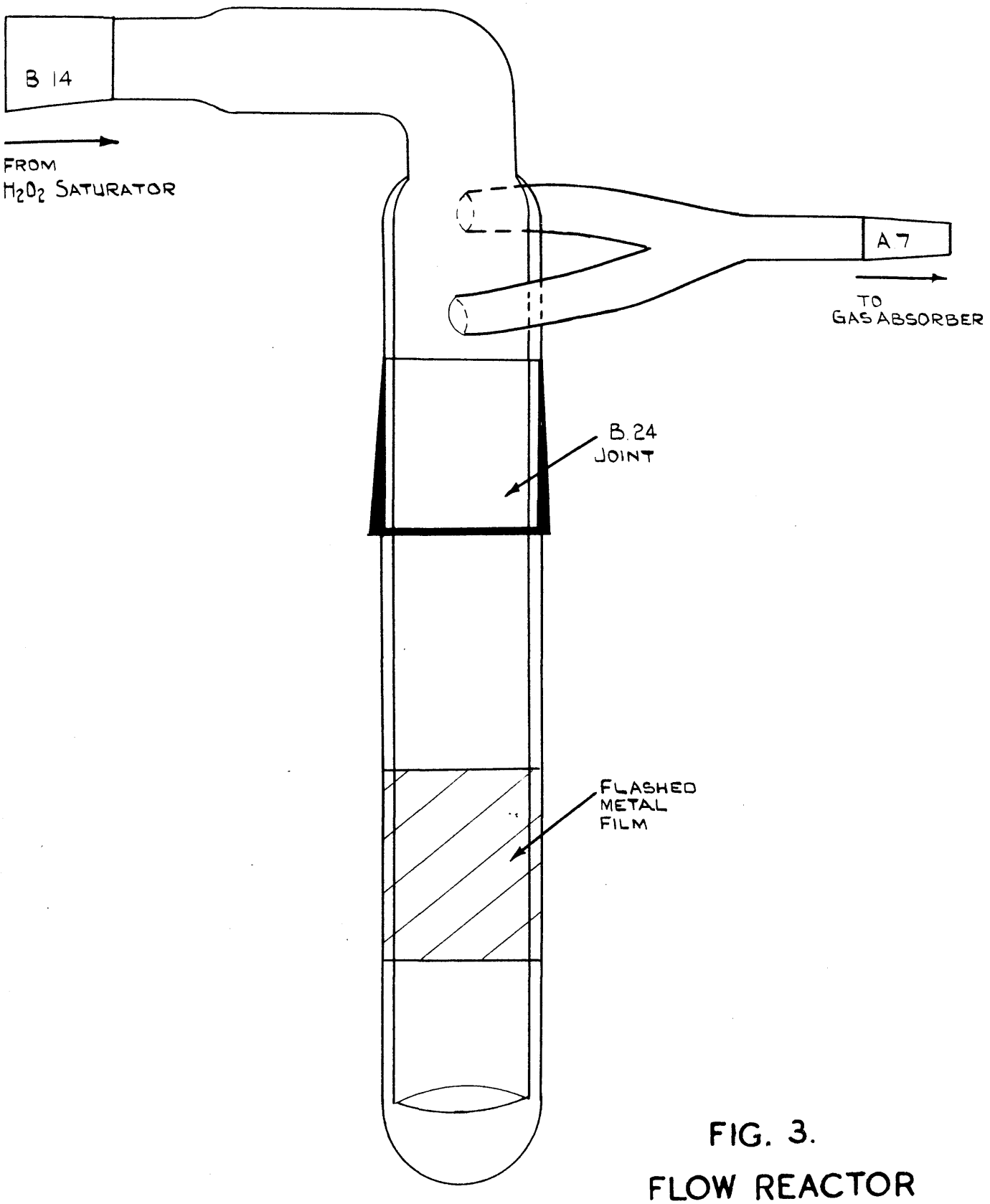



FIG. 3.

FLOW REACTOR
(METAL FILMS)

decomposition of the peroxide.

Streams (1), (2) and (3) were now passed into the common manifold as shown in Fig. 1. Stopcocks were provided in streams (1) and (3). From this manifold the mixed gases passed in a common stream to the preheater via a B10 joint.

(P) The spiral preheater which was a modified C3/12 quickfit condenser with a coil length of two feet. It was used to bring the temperature of the gases up to that of the catalyst, whilst serving also to mix the gases before entering the reaction tube.

Two different types of reaction tubes were used in the experiments. One was utilised in the examination of evaporated metal films and the other for metal oxide, and mixed oxide compressed slips.

The flow reactor for metal films.

This consisted of an 18 mm. internal diameter pyrex tube, bent to a right angle at the vapour entrance, which was coupled to the preheater via a B14 socket (Fig.3.) The tube, 30 cm long, was internally sealed into a B24 socket 4 cm below the bend. This socket formed the head of the reactor and connected to the catalyst chamber by the B24 joint. (The metal oxide film to be examined having previously been deposited on the wall of the chamber as a circular band 5 cm. broad. The bottom edge of which was a distance of 10 cm. from the base of the catalyst chamber.)

The gas stream from the preheater passed into the catalyst chamber through the pyrex tube and came into close contact with the catalyst while flowing through the 2 mm. annular gap. The effluent gas from the reaction was then bubbled into the gas absorbers through the two exit tubes sealed into the B24 head.

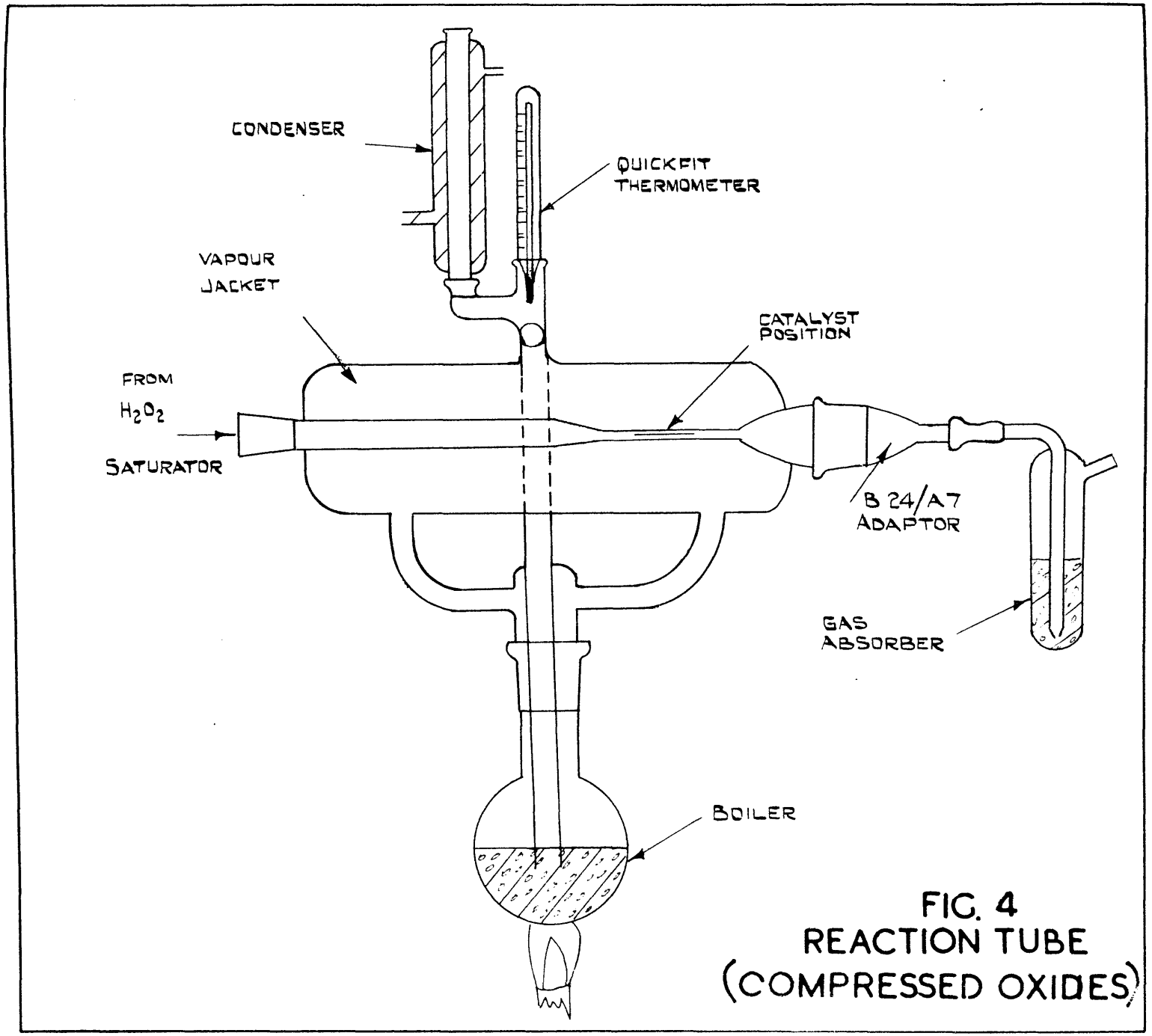



FIG. 4
REACTION TUBE
(COMPRESSED OXIDES)

The unit was immersed in a stirred oil bath to just below the B24 joint. The bath was heated by a 250 watt immersion heater and the temperature controlled by a mercury or toluene regulator connected to the mains through a "Sunvic" relay.

Reaction tube for oxides slips.

It was originally intended to examine the oxide catalysts impregnated on a silica mesh support. Experiments were made in this direction by boiling discs of the support with solutions of certain metal nitrates followed by heating to the oxide. On examination, it was found that this method resulted in irregular coverage of the support by the oxide and it was virtually impossible to prepare reproducible surfaces.

To surmount this difficulty, and to obtain catalysts of similar surface areas, it was decided to use the oxides in some form of compressed plate or slip. The reaction tube was designed accordingly, and the final unit is shown in Fig. 4.

It consisted of a 2 cm. bore pyrex tube 17 cm. long, tapering over 3 cm. to a rectangular cross-section, 1 cm x 0.25 cm x 10 cm. long. This was blown out at the exit to form a B24 socket. The catalyst of dimensions 2.5 cm. x 1 cm. x 0.1 cm. being situated 1-2 cm along the rectangular tube. A vapour jacket enclosed the tube and constant temperatures were obtained by refluxing the vapour of a redistilled liquid, boiling at atmospheric pressure, into the jacket.

The absorber.

The gas from the flow reactor was then passed into a "bubbler" which acted as an absorption unit for the peroxide vapour. These were constructed in pyrex glass, 15 cm. long by 2.5 cm. diameter. The orifice of the

bubbler being 0.5 cm. bore, and its feed-end connected with an A10 socket to the reaction tube via an A10/B34 coupling. The exit tube of the bubblers was open to the atmosphere, thus allowing the nitrogen carrier gas to escape. It was found that only one bubbler, containing 20 mls. distilled water, was required to absorb all the effluent peroxide. When two or more were added in series and the contents analysed by titration with 0.01N $KMnO_4$, no peroxide was detected in any but the first bubbler.

Temperature control.

In experiments with the oxidised metal film catalysts, the reactor tube was fixed in position in a thermostatically controlled oil-bath, preheated to the temperature required. Dry nitrogen was then passed through the system which was allowed to stand for approximately 5 minutes to attain temperature equilibrium before commencing a run. The temperature of the oil-bath was controlled to $\pm$ 0.01°C at temperatures up to 100°C, and over this control was to $\pm$ 0.02°C. Unfortunately, this system did not allow temperature changes to be made as quickly as desired in determining the temperature coefficient. There being a time lag of 5 minutes required to give a steady temperature 20C° higher when making a change.

The temperature control with the slip - reactor was to $\pm$ 0.01°C in the range 38 - 183°C. This was attained by refluxing the middle fraction of the following redistilled ebulliostatic liquids from a 500 ml B24 round bottom flask attached to the vapour - jacket; the boiling points, to the nearest 0.5°C; are given in brackets:-

(1) Ethyl Bromide (38°C) (2) Chloroform (60°C)

(3) Carbon Tetrachloride (76.5°C) (4) Benzene (80°C)

(5) Water (100°C) (6) Xylene (136°C).

(7) Aniline (183°C).

In this system, temperature changes were accomplished in less than 60 seconds by quickly changing from a flask of one liquid to another preheated to near the temperature required. The temperature of the vapour was ascertained from a B14 quickfit thermometer enclosed in the vapour jacket. This was recorded as the temperature of the run which could differ slightly from the above boiling points, due to contamination of the liquids from the drainage of the vapour jacket. It was necessary frequently to redistill the liquids to rid them of this contamination.

With the pre-heater containing methyl alchol boiling at 64°C, supplying a background heat to the peroxide vapour, it was shown by the use of thermistors, that the peroxide stream attained the temperature of the vapour jacket at a distance of 4 diameters along the reaction tube, i.e. 5-6 cm. from the entrance with temperatures up to 100°C and slightly more for temperatures of the higher order. Even at 183°C the peroxide vapour was within 1C° of the catalyst temperature by the time contact was made.

Cleaning glassware.

In all work concerning the flow system extreme care with cleaning had to be taken in all experiments to obtain reproducibility of blanks. Conventional methods of cleaning proved to be unsatisfactory e.g. chromic acid could not be used, as it was shown that glass so treated decomposed $H_2O_2$ vapour, possibly by the formation of an invisible chromic oxide skin

on the walls of the reaction vessel, giving decompositions of up to 5% at temperatures c.180°C. Similarly sulphuric acid was not suitable, presumably because of metal ion impurities in this acid which again cause tube contamination and decomposition of the vapour. Cleaning with caustic alkalis was also attempted, without success, possibly due to an etching attach on the pyrex glass surface exposing impurity occlusions and thus making it less stable to hydrogen peroxide.

An effort to stabilise the reaction tube surface, after cleaning with the above mixtures, was made by treating it with 25% boric acid solution. This gave initially a fairly inactive coating but in about one hour at temperatures $> 100°C$. decompositions of 2-4% of hydrogen peroxide vapour were recorded. Treatment with sulphuric acid and ammonium persulphate, which proceeds through the production of $H_2O_2$, was fairly useful but had to be discarded as sulphuric acid of sufficiently high purity could not be obtained.

The cleaning treatment eventually adopted consisted of an ethanol rinse followed by the addition of concentrated nitric acid, analytical grade. The nitrous fumes produced were allowed to permeate the system, which was later filled with dilute $HNO_3$ and allowed to stand for several hours. This was followed by immersion and rinsing with distilled water, and the glass was finally dried at 100 - 150°C. If necessary the cycle was repeated several times.

After this treatment no decomposition was observed on the glass at temperatures below 136°C and any which occurred between this temperature and 183°C was less than 3.5% and involved a very small correction. Thermal decomposition of $H_2O_2$ vapour was not an important factor since

this does not take place until temperatures of around 600°C are attained (McLane, 29).

Blank Determinations.

The system was first purged with nitrogen with the reactor at the required temperature, in order to remove traces of moisture still possibly occluded in the reaction-tube. This was continued for 30 minutes. The dry nitrogen stream was then stopped and replaced by that from the peroxide saturator.

The flowmeter was quickly adjusted to give the required flow-rate and the apparatus allowed 15 minutes to settle down. The gas absorbers were changed every 5 minutes and the peroxide content of the gas stream determined by a titration with 0.01N $KMnO_4$. Concordant results were usually obtained with successive blanks, but if this was not the case, the apparatus and especially the reaction-tube, was recleaned. The flow-rate was checked when necessary at points between the flow-meter and gas absorber, by the use of a sensitive rotameter which tested for leaks in the system due to faulty joints. Only very rarely was such a leak detected.

A specimen set of results and calculations for blank runs was as follows:-

| | |
|---|---|
| Temperature of Saturator | 15°C. |
| Concentration of $H_2O_2$ in Saturator | 99.90% |
| Flow Rate | 300 mls/min. |
| Sample Time | 5 mins. |

Table 1 shows the experimental figures obtained with these conditions:-

TABLE 1

| Time (mins) | Reaction Tube Temperature ($^{o}$C.). | Titre MLS.0.01N $KMnO_4$ |
|---|---|---|
| 0 | 100 | 0 |
| 5 | 100 | 15.92 |
| 10 | 100 | 15.93 |
| 15 | 100 | 15.94 |
| 20 | 100 | 15.95 |
| 60 | 100 | 15.95 |
| 180 | 100 | 15.95 |
| 200 | 184 | 15.90 |
| 205 | 184 | 15.91 |
| 210 | 184 | 15.90 |
| 240 | 184 | 15.90 |
| 300 | 184 | 15.90 |

At the steady state at 100$^{o}$C.

Wt. of $H_2O_2$ in vapour in 5 minutes $= \frac{15.95 \times 17.01}{100 \times 1000}$

At the steady state at 183$^{o}$C. $= \underline{\underline{2.72 \times 10^{-3} \text{gms.}}}$

Wt. of $H_2O_2$ in vapour in 5 minutes $= \frac{15.90 \times 17.01}{100 \times 1000}$

$= \underline{\underline{2.71 \times 10^{-3} \text{gm.}}}$

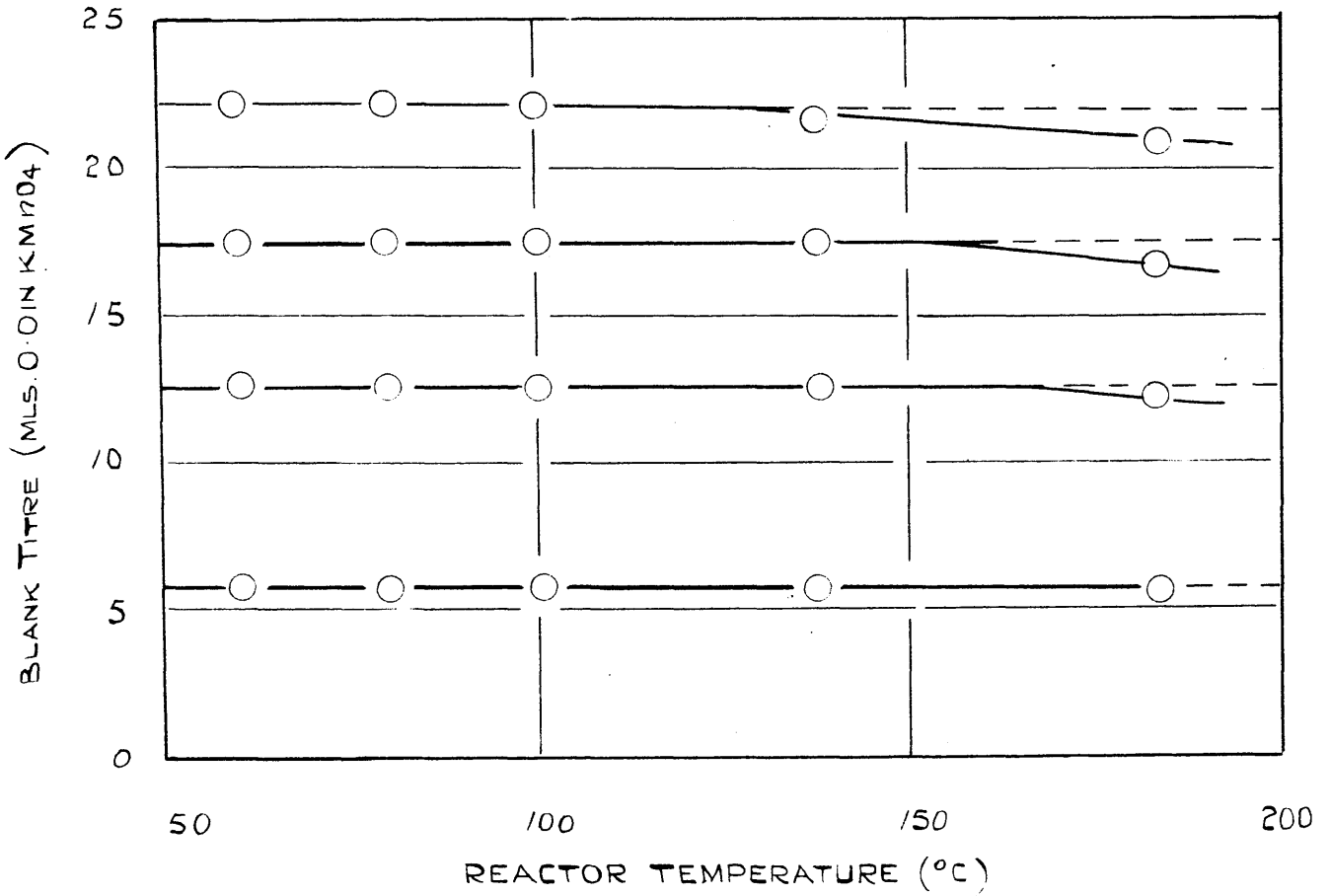
Comparison with theoretical.

Partial Pressure of $H_2O_2$ over 99.90% $H_2O_2$ solution.

$= 0.96$ mm. (Kavanagh, 84)

Wt. of $H_2O_2$ in 1.5 litres $= \frac{0.96 \times 1.5 \times 34.02}{760 \times .082 \times 288}$

$= \underline{\underline{2.72 \times 10^{-3} \text{ gm.}}}$




SHOWING EXTENT OF BLANK
DECOMPOSITION AT DIFFERANT CONCENTRATIONS
– – – THEORETICAL BLANK VALUE
○ EXPERIMENTAL POINTS

FIG. 5.

∴ At the steady state, at 100°C, Blank Decomposition = 0.

and, At the steady state, at 184°C, Blank Decomposition ≃ 0.3%

Fig. 5 shows the deviation of the experimental blank from the theoretical value at various concentrations of $H_2O_2$ in the vapour phase, and it can be seen that the blank decomposition was small in the temperature/pressure region studied i.e. 38-183°C, and 0.3 - 0.96 mm. Hg pressure. The decomposition occurs only over 100°C and increases slightly with rising peroxide concentration. It was generally negligible in comparison to the catalytic decomposition, so that in very many cases it could be neglected entirely. (These blank deviations refer, of course, to the decomposition on pyrex glass).

Efficiency of catalysts.

After obtaining a satisfactory blank, the catalyst was manoevred into the reaction tube with the aid of surgical tweezers, taking care not to damage or break the leading edge of the slip; which was so placed in position as to give 1 mm. clearance between the catalyst and the top and bottom walls of the reaction vessel. When this had been accomplished, the nitrogen flow was switched into the hydrogen peroxide saturator, only a few seconds being required to adjust the flow to the necessary value. When the temperature of the gas stream was tested during this change no fluctuations were observed.

When the $H_2O_2$ vapour had passed over the catalyst for 5 minutes, as timed by a stop-watch, the effluent gas absorber was quickly changed over, and the amount of $H_2O_2$ present estimated by a titration with 0.01N $KMnO_4$. Subtraction of this figure from the blank value gave the amount of vapour

decomposed. These determinations were continued until the steady decomposition value was reached. Generally, this level was attained after 20-25 minutes, and the measurements were continued for 60-70 minutes. If the run was extended to 2 or 3 hours, steady changes in activity of about 1% were sometimes observed. However, slow changes of this nature were not studied in these experiments.

Initial changes of efficiency.

During the first exposure of a catalyst to $H_2O_2$ vapour, the initial fast changes of efficiency were often determined by taking samples of the effluent peroxide vapour every 60 seconds. Changes of absorber tube could be made in about a second and there was negligible disturbance of the flow rate in the change, providing that the volume of water in the absorbers was carefully pre-adjusted.

Determination of reaction order.

The order of the reaction was ascertained by a method involving quick changes of $H_2O_2$ concentration, whilst keeping the flow rate constant. Thus, with a flow rate of 300 mls/min, and a hydrogen peroxide concentration of $C_i$ in the gas stream; several determinations were made in the manner previously described. When a steady decomposition value had been reached, the inert gas flow through the $H_2O_2$ saturator was cut to 200 mls/min. i.e. to 2/3 $C_i$ and the total flow brought back to 300 mls/mm. by the addition of dry nitrogen. Again, when a steady decomposition value was reached 2/3 $C_i \rightarrow$ 1/2 $C_i$ and similarly 1/2 $C_i \rightarrow$ 1/3 $C_i$. This was followed by the reverse procedure, 1/3 $C_i \rightarrow$ 1/2 $C_i \rightarrow$ 2/3 $C_i \rightarrow C_i$, by replacing the dry nitrogen increments with peroxide saturated nitrogen from the $H_2O_2$ saturator. Each of these concentration changes could, with practice, be

completed in 15-20 secs.

Determination of temperature coefficient.

The temperature coefficient of the reaction rate was found by making quick temperature changes within the limits of the decomposition. This was accomplished by switching from one constant-boiling liquid to another, after the steady decomposition limit had been reached at a given temperature. By pre-heating the change-over liquid, the new temperature of the catalyst and reaction-tube was attained within 60 seconds, as recorded on the top thermometer, and by a thermistor attached to the catalyst during test runs at the various temperatures.

The decomposition was allowed to come to a steady value, taking about 20-45 minutes according to the temperature, and the temperature changed to a new value by again switching to a different ebulliostatic liquid. By this method decomposition figures were obtained, in the temperature range 38 - 183°C, for each catalyst studied; thus permitting an evaluation of the temperature coefficient of the reaction rate for each stepwise change.

In the case of the metal films it was more difficult to effect immediate fast temperature changes. Even by employing two hot oil baths it took about 5 minutes to attain the necessary steady values. So in this instance it was not possible to attain the sudden efficiency change in a given temperature interval, as with the other reaction tube.

Effect of oxygen and water vapour on the rate.

In studying the effect of oxygen on the decomposition rate, the method employed was to change completely from nitrogen to oxygen as the

carrier gas entering the storage vessel (R). The change from one gas cylinder to the other was accomplished within 5 seconds, and the time required to give a steady pressure value in the flow system varied slightly between 10-20 seconds. It would be incorrect to say that after a change from oxygen to nitrogen, the total gas flow was immediately composed of only one of the gases; because of the time required to displace the existing gas in the storage vessel (R).

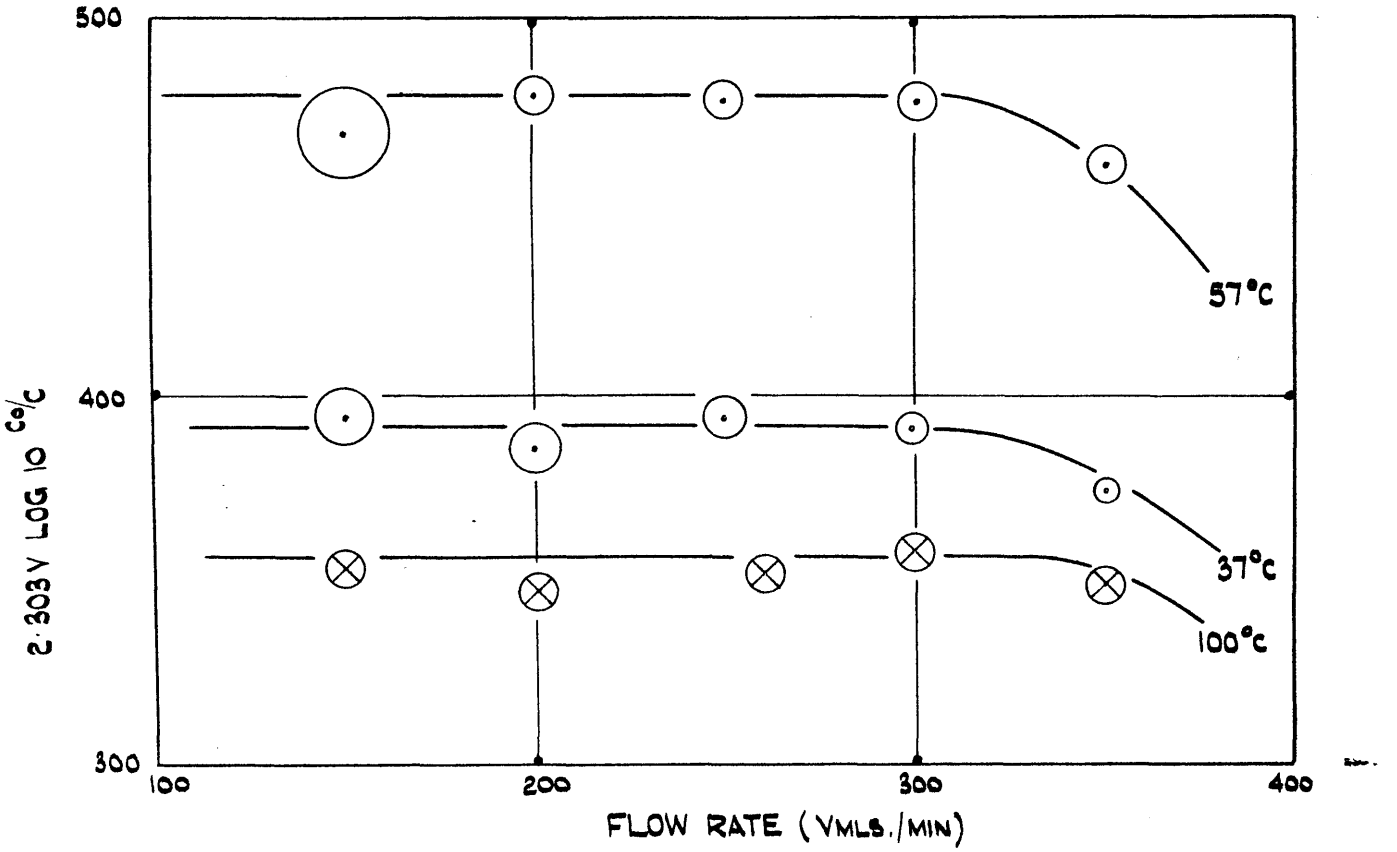
In this instance, and with the water vapour additions, the runs were all carried out with over 99% w/w freshly distilled, unstabilised hydrogen peroxide.

Water vapour was added by passing dry nitrogen into the saturated solution of $Mg\ Cl_2$ at a constant temperature, chosen so that the saturation pressure at atmospheric conditions would not be exceeded. By adjusting the flow of the carrier gas passing into the saturator, suitable increments of water vapour were added in the pressure region 1-16 mm. Hg. The total flow was restored to 300 mls/min. by additions of a fixed amount of peroxide saturated gas and variable quantities of dry nitrogen from the other streams.

Experiments to detect transport control.

The flow rate, dimensions of the reactor, temperature range, and the arrangement of the catalyst were chosen so that surface processes and not gas phase diffusion of $H_2O_2$ to the surface controlled the rate.

If gas phase diffusion was rate-controlling a first order process would be found relating rate of catalysis to gas phase concentration of $H_2O_2$ at a given flow rate. All effective catalysts of the same area would be expected to give the same rate of decomposition. This was, of course,




PLOT OF 2·303 V. LOG 10 Co/c WHERE V. IS THE FLOW RATE. DEMONSTRATES 1ST. ORDER CHEMICAL CONTROL. SIZES OF CIRCLES REFER TO UNCERTAINTY OF DATA.

◯ ZnO/$Mn_2O_3$ ⊗ Ni/NiO.

FIG. 6.

far from being the case. At quite low temperatures the best catalysts could achieve $> 98\%$ decomposition while with the less active ones a much higher temperature was necessary before decomposition could be observed at all. This seemed to provide strong evidence that so long as decompositions were not too close to 100% we could ignore gas phase diffusion as a controlling factor.

Experiments to demonstrate the independence of kinetics on flow velocity were made using gas flows in the region of 400-100 mls/min. at various temperatures. Fig. 6 illustrates the results with catalysts of widely different type, a surface oxidised nickel metal slip and compressed $ZnO/Mn_2O_3$. It is shown that for flow rates between 150 and 350 mls/min the rate of decomposition, at a fixed $H_2O_2$ concentration, is independent of flow rate. As would be expected, above the higher flow limit the fraction of peroxide decomposed for a given time of stay at the catalyst falls slightly, presumably because average $H_2O_2$ molecules make fewer collisions with the catalyst per second than they do at smaller flows, - or put in another way molecules remote from the active surface when the gas reaches the catalyst zone are not able to diffuse into contact before the bulk flow has passed it. At flows slower than the limit a higher decomposition is observed. This suggests that at these bulk flows the time of contact with the catalyst is longer than it appears to be - perhaps due to back diffusion.

(b) Metal evaporation unit.

The technique adopted in the production of metal films was similar to that used by Finch et al. (85) and later by Trapnell (86).

The apparatus shown in Fig. 7 consisted of a three-stage mercury diffusion pump backed by a high efficiency two-stage mechanical oil pump through a $P_2O_5$ trap. The diffusion pump led through two vapour traps immersed in Dewar flasks containing liquid oxygen to the flashing unit attached by a B19 joint.

The flashing unit head was a B24 socket into which two tungsten wires, 1 mm. diameter, were sealed. Both wires were encased in glass capillary tubing. The tubing was held rigidly by glass rods, which served to retain the tungsten wires in position. One wire was 5 cm. shorter in length than the other and was placed centrally in the head. The metal filament to be flashed was linked to the ends of these wires so that deposition occurred radially from the centre, with the catalyst tube surface interposed within the limits of the mean free path of the evaporating systems.

Midway between the flashing unit head and the B19 trap joint, a B14 socket was sealed to take the Pirani gauge head which was connected to an Edwards vacuum indicator. The current used in the evaporation was supplied by a bank of accumulators which were connected to the tungsten terminals via a rheostat and ammeter.

Evaporation technique.

The apparatus was evacuated for 16-20 hours accompanied by intermittent baking-out, (heating with a bunsen to the point of collapse). This enabled a vacuum better than $10^{-5}$ mm. to be maintained when depositing the films. In all cases the deposition surface was cooled by liquid oxygen. This procedure was intended to avoid preferentially oriented films (Beeck, Smith and Wheeler (89) ).

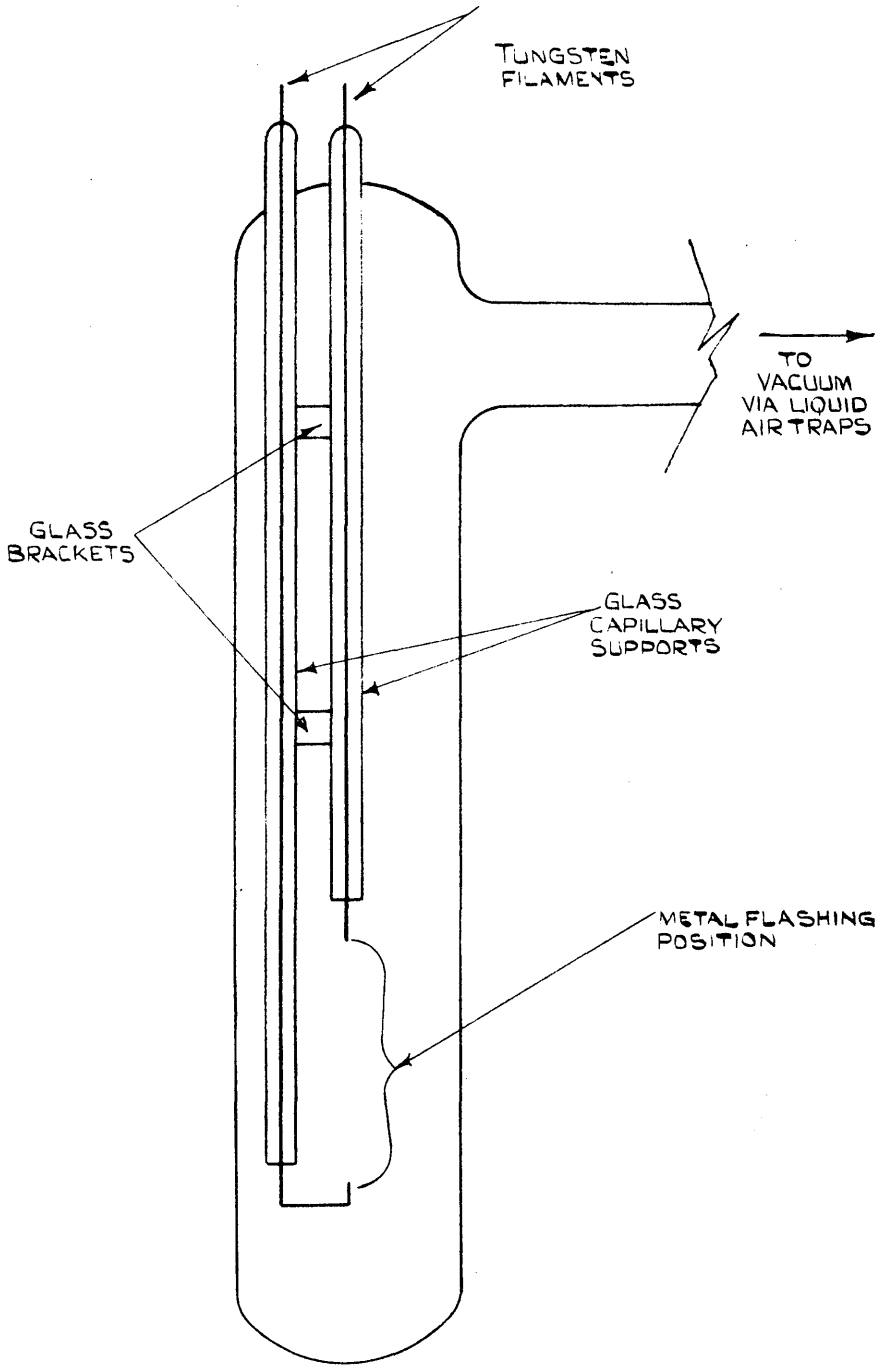



FIG. 7.
METAL FLASHING UNIT

The film thickness of the metals deposited were in the region 5-10 $\mu$ as calculated by dissolving the film in acid and analysing for Ni by conventional methods. Deposition was completed in 15-20 secs. with a D.C. current of 5-7 amps. Films of nickel deposited in this fashion were transparent but on admission of air became black due to the formation of an oxide at the surface. Air was admitted to the system at - 183°C, which was then quickly brought to room temperature.

By this method films of many metals were spluttered, either as "specpure" wires or as electrolytic deposits on a clean tungsten filament, 0.01 mm. diameter.

(c) Magnetic Susceptibility Balance.

The determinations were made with a Sucksmith type balance (87) as used also by Dilke, Eley and Maxted (88).

The apparatus is shown in Fig. 8, and was constructed from simple materials. It consisted of a low extension micro-balance made from a circular strip of phosphor-bronze which was 38, 42 or 46 s.w.g., according to the sensitivity required. The width of each strip being 2 mm., bent into a circle of 5 cm. diameter. The ring was supported at the top by a slit in a brass rod and was enclosed in a brass box, 10 cm. x 10 cm. x 13 cm., with glass windows in three sides. Light from a galvanometer lamp was reflected from mirror B to mirror A and then on to a vertical scale at the focussing distance of 1 metre, by a system of plane mirrors outside the box. A light mica scale pan was attached to the lower extremity of the ring from which the specimen was suspended by means of a fine glass or nylon thread.

The specimen was packed into a thin walled glass phial, 7 cm. long

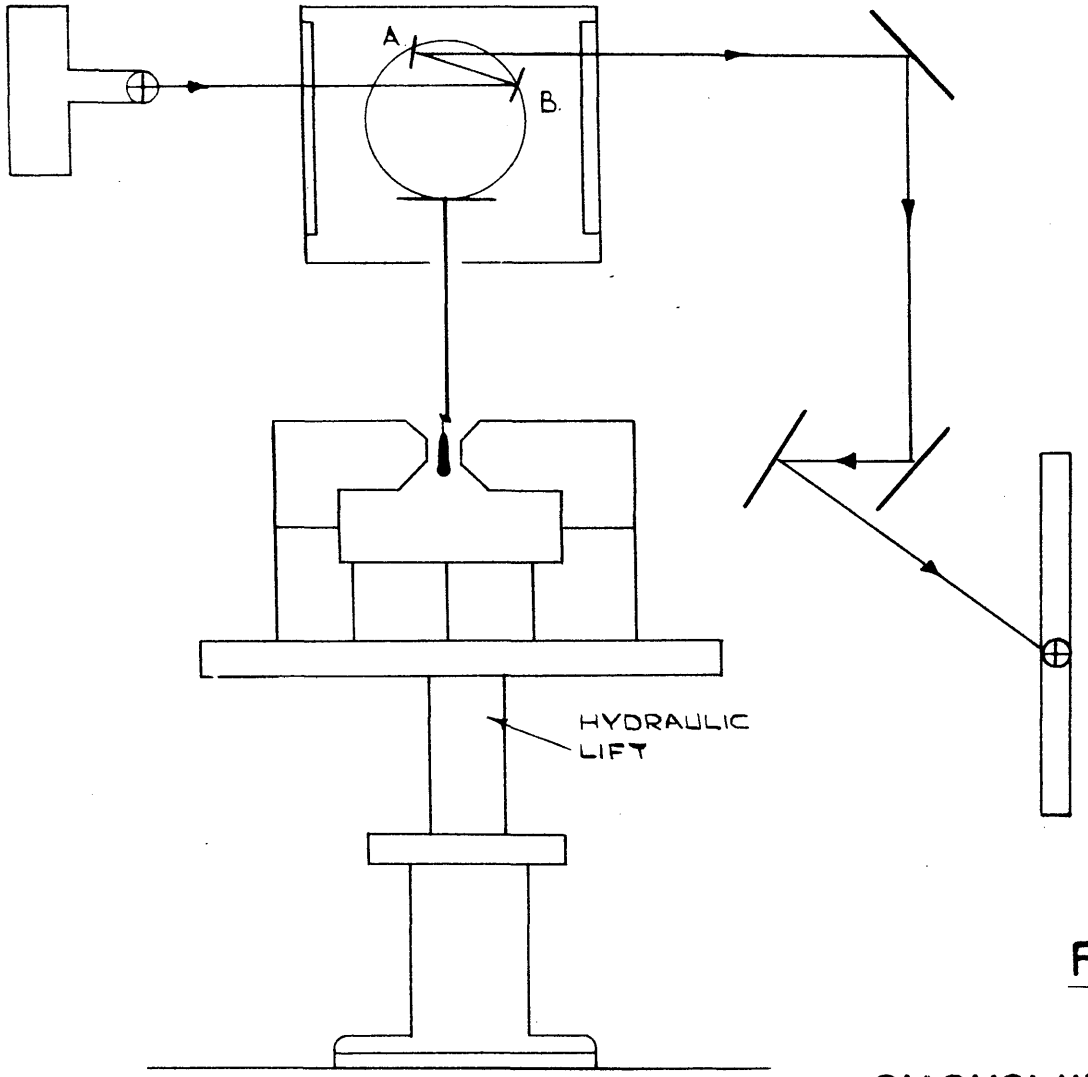



FIG. 8.

SUCKSMITH BALANCE

x 1 mm. diameter of uniform cross-section. The materials were thoroughly ground in an agate mortar to pass 300 B.S. sieve and carefully packed into the phial by tapping on the bench several hundred times in order to minimise discrepancies in packing density, which is the principle source of error in this method.

Since an electro-magnet was not readily available the measurements were made with permanent magnets of field strengths 10,600 oersteds and 1,500 oersteds respectively. These were obtained from W^m. Jessop & Sons Ltd., Sheffield, and were manufactured in the sintered "Alcomax III" alloy.

By means of a hydraulic lift (a modified lorry jack), the magnet was smoothly manoeuvred into position, and the maximum pull, (when the tip of the specimen was at the middle of the pole gap), was determined from the galvanometer scale deflection. This was repeated until a constant deflection was obtained. The specimen was prevented from attaching to either pole by means of two fine nylon retaining threads attached to the top of the magnet by a mica support.

The apparatus was calibrated with a saturated solution of ferrous ammonium sulphate, for which X (magnetic susceptibility/gm)

$$= \frac{9,500 \times 10^{-6}}{(T + 1)} \quad \text{c.g.s. units.}$$

where T = $^{o}$K. In addition, the susceptibility of various pure oxides of known values was determined at the two field strengths and agreed to within 1% with I.C.T. data.

The measurements were all made at room temperature and the final value for each system was taken as being the average given by three separately packed specimens. The X values may be criticised, on the

grounds that determinations should have been carried out at different temperatures to obtain susceptibility isotherms (Selwood, 67). This is a useful method of detecting the presence of paramagnetic impurities but was rather out with the scope of this work. It was felt that careful measurements at two field strengths would be sufficient to characterise each substance, and a graph of X against 1/H would indicate whether any ferromagnetic impurities were present.

The calculation of X was carried out in the following manner:-

Magnet moment induced/cc = kH.

Where k = volume susceptibility and H = field strength.

Magnetic moment induced in volume $\delta v$ = $kH\delta v$.

Now, force acting on $\delta v$, $\delta F$ = moment $\cdot \frac{\delta H}{\delta l}$

(Since $\delta v = A \delta l$) = $kHA\delta H$

= $\underline{\underline{\frac{1}{2}kA\delta H^2}}$

Integrating over the whole length (l) of the specimen, we have:-

$$\int_0^l \delta F = \tfrac{1}{2} AK \int_{H_1}^{H_2} \delta H^2 \quad \text{(Since } H_2 \gg H_1\text{)}.$$

i.e. $F = \frac{1}{2} kAH^2$. (Since $H_2 \gg H_1$).

But $F = \delta wg$, where $\delta w$ = pull in gm. Weight and X (gm. susceptibility) = $k/\rho$ ($\rho$ = density of specimen)

$\therefore$ $\underline{\underline{X = \frac{2\delta wgl}{H^2 W}}}$ (W = Weight of specimen)

(d) Surface area apparatus and measurement.

The apparatus used is shown in Fig. 9 and was a modified version of that proposed by Duncan (76) and Wooten and Callaway-Brown (77). Mercury

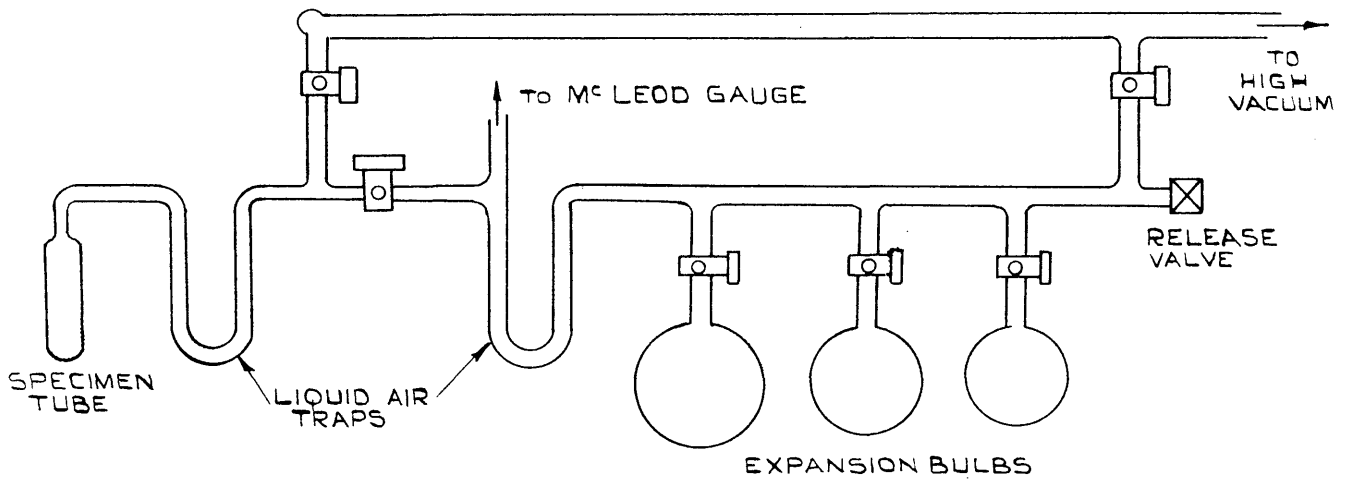



FIG. 9

SURFACE AREA APPAR-TUS

seals being replaced by vacuum stopcocks, and a series of three expansion volumes introduced.

The measurements were made with ethylene adsorption at - 183°C, and preliminary trials were carried out to find a suitable stopcock grease which would not absorb this gas. Various commercial high vacuum lubricants were used, as were mixtures composed of fused dextrose/glycerol and mannitol as recommended by Tyrer (90). These were applied without success, whilst although very little ethylene absorption was detected, the greases were liable to retain moisture and also to carbonise whilst flaming out the apparatus.

This difficulty was finally overcome by using a fluorocarbon grease, kindly presented by I.C.I., Widnes. For example, on allowing vapour/grease contact for 12 hours, the pressure in the system remained constant at $3.5 \times 10^{-4}$ mm. Hg, as measured on a McLeod gauge.

The apparatus was evacuated by a high efficiency mercury diffusion pump backed by a mechanical oil pump, attached to the vacuum manifold through two liquid air traps. The total volume of the apparatus was 2,100 c.c. and an evacuation to $8.2 \times 10^{-6}$ mm. Hg pressure when left for 60 hours changed to $7.9 \times 10^{-5}$ mm. Hg, a reasonable leakage for a vacuum apparatus of this size and one which would not interfere with the surface area measurements.

The volumes of the various parts of the apparatus were determined from that of the McLeod gauge - using the bulb volume of the McLeod as a gas pipette. The McLeod bulb volume was previously calibrated against a flask attached to the manifold which, in turn, had been calibrated by weighing the mercury required to fill it.

A 500 ml. flask containing ethylene, (99% purity, I.C.I.) kept over dry sodium or $P_2O_5$, was connected to the manifold via the release valve, the expansion bulbs and manifold having previously been subjected to a hard vacuum accompanied by flaming for 45 minutes. When this was complete the bulbs were closed to the manifold and a liquid oxygen trap placed around U-tube. The $C_2H_4$ was then allowed to issue into the system and was successively evaporated, condensed and pumped off to remove entrapped air. Finally, the ethylene was admitted to the expansion bulbs which were then closed to the manifold.

The measurements were made by having a liquid oxygen trap at a constant level around the specimen tube. The whole system was evacuated and a very small amount of $C_2H_4$ allowed into the manifold (not sufficient to reach the condensation pressure) and the pressure measured on the McLeod gauge by a cathetometer reading to .001 mm. Tap A was then opened and the $C_2H_4$ allowed into the specimen side of the system. After about 15 minutes, tap A was closed and the McLeod gauge reading taken. The adsorption was then found by the usual difference method calculated from the total gas charge and the quantity of gas in the gas phase.

The gas charge was checked at the end of each run by measuring the pressure with the specimen at room temperature. According to Duncan (76), with this system errors due to thermal transpiration are generally negligible as is the Knudsen pressure drop through liquid oxygen cooling. No minor gas law or glass adsorption corrections were applied; the absolute accuracy of the surface area figures being probably of the order of $\pm$ 15%.

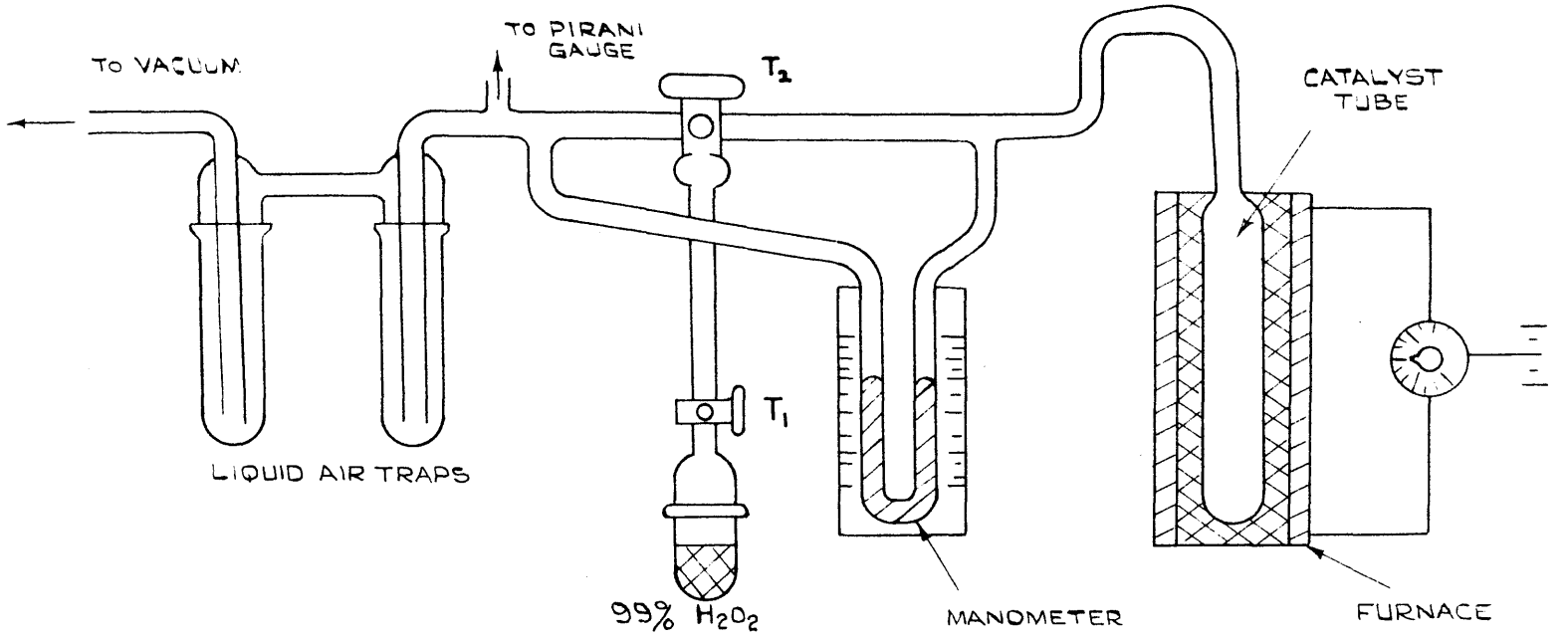



FIG 10

STATIC SYSTEM

(e) Static system.

The equipment is shown in Fig. 10 and was of simple design, constructed in pyrex glass. It consisted of a catalyst chamber, A, 20 cm. long x 2.0 cm. internal diameter, jacketed in an aluminium tubular furnace, F, which was supplied from the mains via a "Sunvic" input control, the temperature being registered by a standard chromel/alumel thermocouple tightly jammed between the catalyst chamber and the close-fitting furnace. The chamber was sealed to the vacuum line, in order to dispense with greased joints.

The oil-manometer, M, contained freshly distilled dibutyl phthalate and the peroxide reservoir, C, 12 mls. $H_2O_2$ (>99% w/w). The vacuum was supplied by a similar unit to that described under metal films and was registered on a Pirani gauge.

Method of measurement.

The $H_2O_2$ in C was frozen by liquid oxygen, melted and then pumped off to remove entrapped oxygen. This cycle was repeated several times. (The system was previously baked out and evacuated to $5.0 \times 10^{-4}$ mms Hg).

The peroxide reservoir was then brought to 20°C, tap $T_1$ opened and the vapour allowed to escape into the volume between $T_1$ and $T_2$. Three-way tap $T_2$ was then opened to allow the gas into the reaction chamber, and the decomposition followed by the pressure change registered on manometer, M. Readings being taken every 20 seconds.

It was originally intended to deposit the catalyst on the walls of the reaction chamber in the form of an oxide film, to obtain a reproducible surface. However, in the experiments reported the catalyst was 0.5 gm. oxide ground to pass 300 B.S. sieve, dusted over the inside of the tube

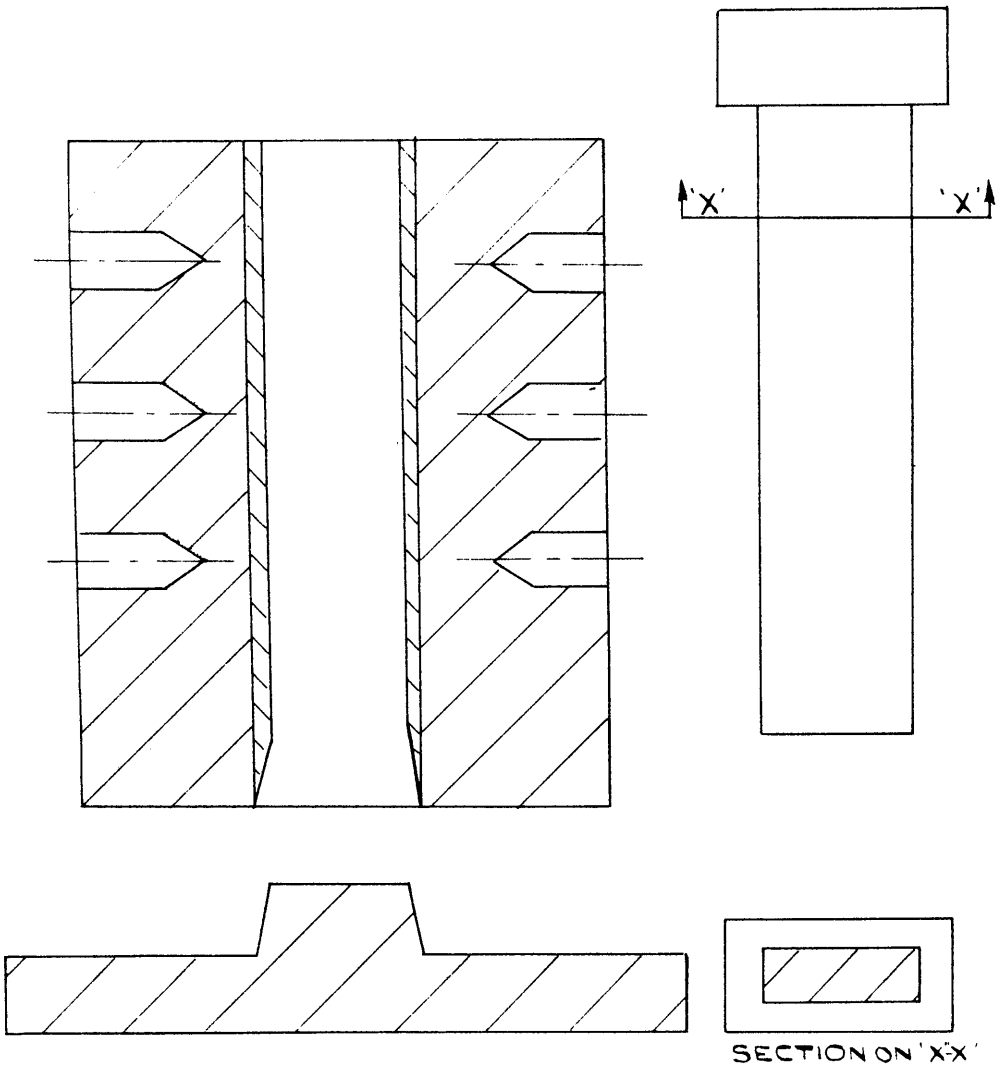



FIG 11

PELLET PRESS, ANVIL & PLUNGER

with slight excess at the bottom of the vessel. The investigations were carried out in the range 30 - 120°C and 0.5 - 2 mm. Hg pressure of $H_2O_2$ vapour.

The unit was constructed towards the end of this research period, in order to compare the efficiencies of high activity catalysts in a static system with that found by the flow method, and so to examine the possibilities of obtaining a correlation with other workers (34, 35) on similar static systems with inactive catalysts.

(f) Pellet press.

Since the single oxides and mixtures were to be examined as compact slips of material, a suitable pellet press had to be constructed for this purpose. Considerable difficulty was encountered in making the die, and many designs were experimented with, in this department and also by the Admiralty, T.E.E., Greenock, whose assistance was most valuable in arriving at the final form of press.

It was found that a pressure of 17.5 tons/sq. ins. was required to give a compact slip of material without using an adhesive. At this pressure difficulties arose through the buckling of the plunger and wear of the inside of the die. The press eventually used is shown in Fig. 11 and was constructed in this College. The main body being of mild steel, the plunger, anvil and four inserts being made of a high carbon, chrome steel. This was used to press the dry material into slips, 2.5 cm x 1 cm x 0.1 cm., which were used in the flow apparatus.

The press was thoroughly cleaned after each use with an abrasive, followed by a thorough water rinse and drying with acetone. The pellet surface was at first gently rubbed with filter paper in order to remove

any possible contamination due to contact with the steel plunger. It was also found that when a slip was pressed between sheets of "Fluon" no difference was observed in the catalytic activity. Thus by adopting stringent cleaning procedures, pellet contamination was so negligible as to have no effect on the catalytic performance.

(g) Agate mortar.

This was a mechanical mortar driven by a 0.25 H.P. motor, manufactured by Thos. Dryden and Sons, Preston, and kindly loaned for the purpose of this research by Admiralty Materials Laboratory, Holton Heath, Dorset. It was used in grinding oxides to a uniform particle size and also served to provide an intimate mixture of two oxides by grinding together.

The mortar capacity was 5 gm. and in 12 hours grinding, gave a range of particle size from 1-5 $\mu$, starting with $Al_2O_3$ of 34 B.S. sieve. To give the same reduction ratio with PbO, $Co_2O_3$ etc. a time of 7-8 hours was required. The mortar was thoroughly cleaned after each run by scrubbing with water and detergent, then finally washed and dried.

(2) MATERIALS

(a) Hydrogen peroxide.

This was Laporte's stabiliser-free H.T.P. (High Test Peroxide) supplied at 86 - 90% w/w. In experiments involving additions of water vapour, and where relatively high concentrations of peroxide vapour, c.1 m.m., were required in the gas phase; the $H_2O_2$ was concentrated by distillation in the apparatus of Fig. 12.

800 mls. of unstabilised H.T.P. were distilled using a straight tube reflux column insulated with quartz wool, at 55-65°C and 72 mm. pressure. The peroxide distillate was condensed in a flask cooled by an ice/water mixture. The oil pump was protected by a drying tower containing calcium chloride and glass wool, and by another column of quartz wool impregnated with $Ag_2O$ and $KMnO_4$ to decompose any peroxide vapour liable to be drawn into the pump. The apparatus was constructed in pyrex glass and the evacuation tubing was entirely in thick-walled p.v.c.

Each distillation lasted six hours and resulted in a concentrate of 97 - 98% peroxide as determined by refractive index and titration with standard $KMnO_4$. About 60 mls. of concentrate was obtained from each run. When 300 - 350 mls of this concentrate was collected it was concentrated in the same apparatus until an $H_2O_2$ fraction was obtained for which $n_D$ = 1.4066 at 25°C. This corresponded to 99.9% $H_2O_2$ (Giguère and Geoffrion (91), and Wynne - Jones et al (92). The strength of this peroxide was checked from time to time by permanganate titration, and it was found that the concentration did not alter by more than 0.5% on standing for 4-5 months. It was found also that during use in the saturator the

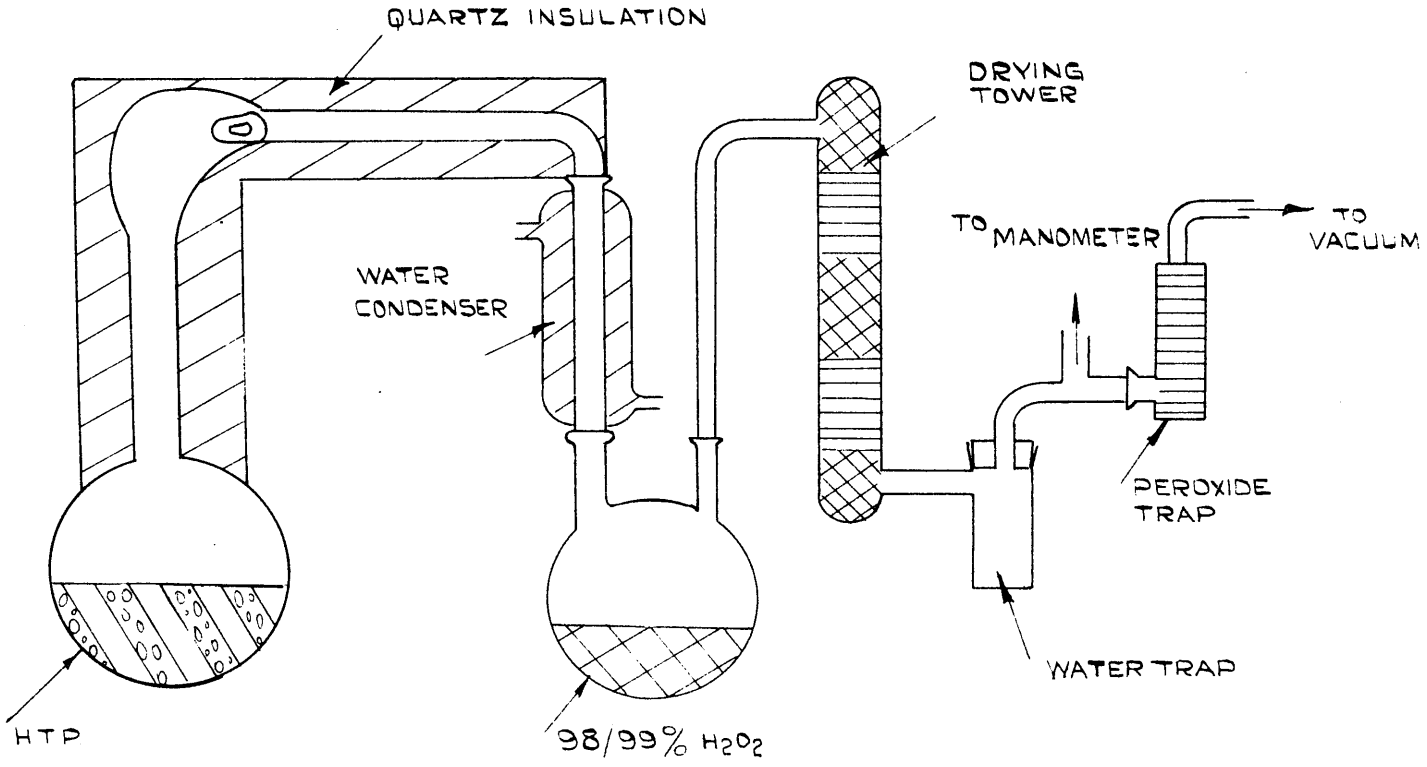



FIG 12

HYDROGEN PEROXIDE CONCENTRATOR

concentration of the $H_2O_2$ solution was kept well up. This was because any tendency to decompose was balanced by the slight fractionation which occurs during passing of the nitrogen.

(b) Catalysts.

These were of three types viz:- Metal slips, bulk oxides and evaporated films.

(i) Metal slips.

"Specpure" metals were purchased from Johnson Matthey & Co., in a form cut to fit the reaction tube. The method of surface cleaning and preparation differed for each material examined and was as follows.

(a) Fe. The "specpure" iron plates were etched with concentrated HCl, and chemically polished with Marshall's solution, i.e. a warm solution containing 1.5 mls. H.T.P., 2.5 gms. oxalic acid and 1 drop conc. $H_2SO_4$ in 100 mls. water, then washed carefully in distilled water, dried, and heated in an oven for one hour at 120°C. This would result in the formation of a film of $FeO/Fe_2O_3$, c.200A° thick, as the surface oxide. Further ocidation to $Fe_2O_3$ takes place at temperatures above 200°C as has been shown by Nelson (93).

(b) Ni. This was employed as a sheet of "specpure" metal, i.e. purity greater than 99.99%, and was degreased in benzene, washed in distilled water and heated in an oven at 120°C for one hour. The oxide film was considered as NiO approximately 50A° thick, similar to that found by Rhodin (94) on copper.

(c) Al. This was cut from a sheet of electrolytic aluminium of 99.9% purity. It was rubbed down with fine sand-paper and then etched with dilute nitric acid, washed, dried with filter paper and heated in an oven

at 120°C for one hour. This results in an oxide film of optimum thickness 80A°, consisting of $Al_2O_3$ or partially hydrated $Al_2O_3$.

Aluminium metal was also treated in hydrogen at 600°C in a tubular furnace for 6 hours and quickly quenched before using in the flow system.

(d) Co. The surface of the"specpure" cobalt plate was prepared in an analogous manner to the Ni above and was considered to have a similar oxide surface film.

(e) Sn. The tin plates were made by melting A.R. tin granules, moulding and machining to slip dimensions. They were then rubbed down with fine sand paper, washed, degreased and dried at 120°C. The surface was then considered to be covered with a film of $SnO_2$.

(f) Ag. This specimen was 99.9% silver and was treated with dilute $HNO_3$, washed and dried at 120°C for one hour. This would result in a surface covered with $Ag_2O$, about 100-200A° thick (Cabrera and Mott, 41).

(g) Cu. The surface of the "specpure" slip was prepared as in (b) and (d), avoiding the use of $HNO_3$ which oxidises the surface to CuO. The oxide film would be $Cu_2O$ and approximately 60A° thick as shown by Rhodin (94), and in previous work in the laboratory by Nettleton (96).

(h) Mn. Owing to the difficulty of obtaining this metal of high purity in a form suitable for examination in the flow system, it was used as a slip with a copper content of 8%, which is less brittle than the pure metal. The surface was smoothed with fine sand paper, treated with dilute $HNO_3$, washed and dried at 120°C.

It will be clear from the above that the metals were all covered with that oxygen layer which would be formed by standing or heating in air for a

short time. The films would normally be protective i.e. they would not tend to increase much under normal conditions.

(ii) Oxides.

The method of preparation of an oxide catalyst is very important. Attention must be paid to the temperature at which the catalyst is prepared, the period of time that the catalyst is held at this temperature, and the gas atmosphere in the furnace (Hüttig and Heinz, 97). A catalyst is often most active in a reaction if it is prepared in the gaseous atmosphere in which it will be used catalytically as has been shown by several investigators (21, 73).

Time and method of cooling after heat treatment will also be important factors. A different active state will result if a catalyst is allowed to cool slowly, than if the defects are "frozen" into the lattice by quenching (Nizboer, 98). In addition to heat treatment, the mode of initial preparation and admixture of the two oxides is important. Such features as particle size and method of mixing (as powders or by co-precipitation) can also be varied.

In the experiments reported a mechanical mixing procedure was adopted. Samples of the divalent oxides were either prepared by decomposition of the A.R. nitrates etc., or by precipitation of the hydroxides, and ignition to the oxide. The oxides thus prepared were ground in an agate mortar to pass 300 B.S. sieve.

(1) $Mn_2O_3$ was prepared by ammonia precipitation of the hydroxide from a 50% solution of A.R. manganous nitrate. The precipitate was washed with distilled water, boiled and filtered several times, then dried at 150°C.

This product was then ignited in a furnace in a flowing oxygen atmosphere at 600°C for 40 hours. Subsequent analysis (by the bismuthate method) showed 99% of the trivalent oxide. The change $Mn_2O_3 \rightarrow Mn_3O_4$ only takes place at 1000°C, and below this temperature $Mn_2O_3$ will result from ignition of any manganese oxide in air or oxygen.

(2) Nickel oxide presented specific difficulties in preparation since it readily occludes oxygen into the lattice and has been reported to exist in many modifications (99). It is now accepted that the structures $Ni_2O_3$, and $Ni_3O_2$ do not exist and that anomalies in the literature may be explained by assuming a rhombohedral unit cell in certain high temperature preparations (100). Previous investigators (101) made no allowance for the presence of chemically bound water in low temperature preparations of the oxide from $Ni(OH)_2$.

The oxide was prepared by ignition of the A.R. nitrate in air, followed by controlled heating for 6 hours at 400°C. This removed all traces of chemically bound $H_2O$, and the oxide was then ground to pass 300 B.S. sieve. The resulting "black" NiO was analysed by the dimethylglyoxime method and corresponded to the formula $NiO_{1.165}$, or approximately 12% excess oxygen.

When this substance was fired in air at 800-900°C for 10-12 hours, "green" NiO resulted which on analysis showed a stoichiometric ratio of nickel to oxygen. Magnetic susceptibility and X-ray determinations were made on these oxides and the results are discussed later.

(3) $Dy_2O_3$ This oxide was obtained from Johnson Matthey & Co., and was of 99.9% purity.

(4) $Al_2O_3$. This was prepared by precipitation of $Al(OH)_3$ by ammonium hydroxide from a solution of the A.R. nitrate. The precipitate was boiled and washed several times and calcined at 900°C to give $\alpha$ - $Al_2O_3$ in the manner prescribed by Day and Hill (102).

(5) $La_2O_3$. and (6) $Ga_2O_3$. These were prepared by high temperature ignition of the "specpure" nitrates. The resulting white, homogeneous powders were then stored in an evacuated desiccator, over $P_2O_5$, until required.

(7) $CoO/Co_2O_3$. Cobalt oxide was prepared by "ignition of A.R. $Co(NO_3)_2 . 6 H_2O$ at 1000°C in air. This results in the formation of a black powder, which is considered to be $Co_3O_4$ with the spinel structure (103).

(8) $Fe_2O_3$. The oxide was prepared by adding ammonia and ammonium chloride to a solution of A.R. $FeCl_3$. The precipitated hydroxide was filtered, boiled and washed several times, dried in an oven at 130°C, and finally ignited to the reddish-brown oxide at 700-800°C in a tubular furnace.

(9) CuO. This was prepared by low temperature (c.450°C) ignition of basic copper carbonate. The resulting black oxide being stored in a desiccator until required.

(10) PbO and (11) ZnO. Yellow lead oxide and white zinc oxide were prepared by ammonium precipitation of the hydroxides from solutions of the A.R. nitrates. The precipitates were treated as in (8) above, followed by heating in air in a silica crucible to give the oxides.

(12) MgO. This was used as the A.R. oxide (Hopkins and Williams, Ltd.) and was simply heated in a furnace at 500°C to expel any $H_2O$ or $CO_2$ possibly present and then quickly cooled, and preserved in a desiccator.

(13) CdO. Cinnamon - brown cadmium oxide was formed by ignition of A.R. $Cd(NO_3)_2.4H_2O$ in air at 300-400°C. It was also prepared by ignition of the A.R. carbonate at the same temperature, and as A.R. CdO as supplied by Hopkins and Williams, Ltd.

(14) $Li_2O$. The white powder was prepared by decomposition of the A.R. carbonate at 800°C in a stream of hydrogen, and stored in a desiccator over $P_2O_5$.

(iii) Metal films.

The metal films were prepared by flashing the metal from a "specpure" wire, or from an electrolytic deposit on a clean tungsten filament. The technique used was described under apparatus. The films flashed were of Cu and Ni, thicknesses 5-12 $\mu$, and were all deposited onto a surface cooled in liquid oxygen to avoid preferential orientation of specific crystal planes.

(iv) Equimolar mixed oxides.

The mixed oxides based on $Mn_2O_3$ were heat treated, after mixing and grinding for 5-6 hours, in a mullite tubular furnace at a controlled temperature in a pre-fired mullite boat. The heat treatment lasted for 6 hours in an inert atmosphere.

The spinel-type systems based on CuO were prepared in a similar fashion only differing in that the sintering was carried out in air.

(v) Trace impurities.

The series of mixtures containing small percentages of foreign cations were prepared by intimately mixing the required amounts in an agate mortar for 3-4 hours and firing in air for six hours at 600°C. By this method the impurity is dispersed into the "mother" oxide, although the dispersion may not necessarily be evenly distributed throughout the lattice.

RESULTS.

(1) General.

In the experimental section, results were reported in support of the claim that with all the catalysts(even the most active ones), the decompositions are controlled by a surface process and not by gas phase diffusion. Accordingly, the following results are displayed in terms of a heterogeneous chemical reaction.

The two types of measurement, based on flashed films on the one hand, and metal and compressed oxide slips on the other, represent two distinct flow patterns and the results will not be compared quantitatively. However, within each series the flow characteristics of the system (contact time, type of flow) are constant between one catalyst and another, and it will therefore be considered valid to compare the catalysts on the basis of the decompositions at given temperatures and the temperature coefficient of the decomposition.

The calculation of the velocity constant, k, and the derived value $E_A$, the energy of activation, depend on knowledge of the order of the reaction and on other factors dealt with more fully in the discussion. Here, however, the method of determining the order and $E_A$ will be given in detail.

(a) Determination of Reaction Order.

Definition of "fraction decomposed", D.

Let the concentration of $H_2O_2$ vapour in the gas stream before reaching the catalyst = $C_i$ mols/litre.

Concentration of $H_2O_2$ vapour leaving the catalyst

$= C_1 = fC_i$ mols/litre.

where f $(0 < f < 1)$ is the fraction of vapour undecomposed.

We define $D = (1 - f)$ as a measure of catalyst activity.

If the titre in 0.01N $KMnO_4$ observed for a 5 minute absorption test is $\chi$ mls without the catalyst. Then:-

$$Ci = \phi \chi, \text{ where } \phi \text{ represents}$$

the analytical factors.

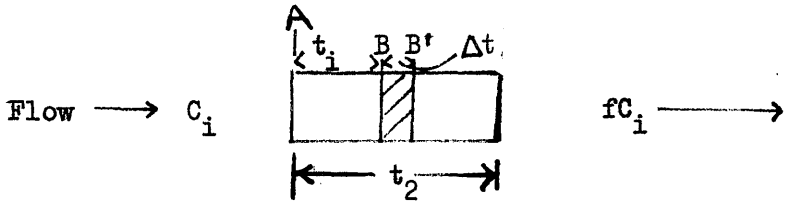
If y is the titre at a given time during the catalysis run, then:-

$$fC_i = \phi y$$

and thus $f = y/\chi$

and $D = \frac{\chi - y}{\chi}$

Kinetic treatment.




Consider the gas flow past the catalyst in the form of a rectangular area as in the sketch. This will approximate quite closely to the actual conditions with slips. It is assumed that gas/solid equilibrium at any zone such as BB' is completely attained.

The time taken by the flow front to pass from A to B = $t_1$

" " " " " " " " " " B to B' = $\Delta t$

If c is the average concentration in the increment of volume represented by the position of the flow front between B & B'. Then for first order kinetics if $\Delta c$ represents the concentration change in the time $\Delta t$, we state:-

$$-\frac{\Delta c}{\Delta t} \simeq -\frac{dc}{dt} = k_1 c$$

Integrating and assuming that it is valid to include in $k_1$ any factors associated with changes in surface itself along the slip, we have

$$- \ln C = k_1 t + \text{constant.}$$

where t is the time of flow across the catalyst to the point at which the concentration is C. The constant may be evaluated, since when

$$t = 0,\ C = C_i \text{ and constant} = - \ln C_i.$$

Also, when $t = t_2,\ C = fC_i.$

$\therefore$ Over the whole length of the slip from t = 0 to $t=t_2$, we have:-

$$\ln \frac{Ci}{fC_i} = k_1 t_2$$

$$\text{i.e. } k_1 = \frac{2.303}{t_2} \log \frac{1}{1-D} \qquad (1)$$

Since $t_2$ is a constant for a given flow rate, if first order kinetics obtain then D, fraction of $H_2O_2$ vapour decomposed, remains constant for any value of $C_i$.

This may be represented graphically by plotting $C_i$ against f $C_i$ (or x against y). For first order kinetics the points will all lie on a straight line passing through the origin as illustrated in Fig. A.

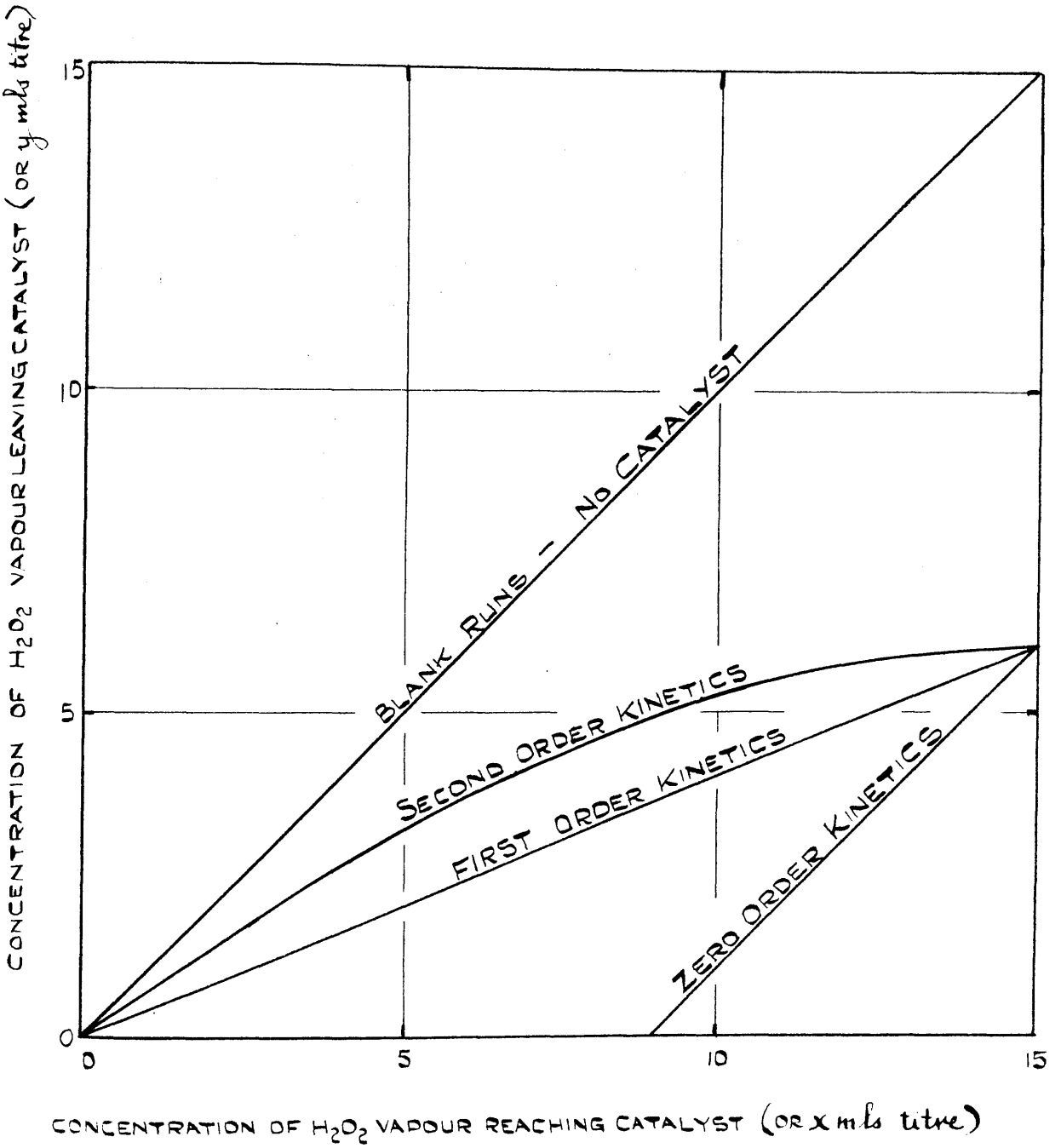
For zero order kinetics:-

$$- \frac{dc}{dt} = k_o$$

i.e. the decomposition rate is independent of the peroxide concentration. It follows that: $Ci - C = k_o t_2 = \text{constant.}$

$$\text{and } DC_i = \text{constant.}$$

showing that D varies inversely with Ci. Zero order kinetics would appear on the graph, Fig. A, as a series of points on a line parallel to that for




THEORETICAL CURVES, SHOWING RELATIVE POSITIONS OF SECOND, FIRST AND ZERO ORDER PROCESSES.

FIG. A.

the blank (not passing through the origin).

For 2nd. order kinetics the fraction of the $H_2O_2$ decomposed will increase with $C_i$ in a rather complex fashion so that in changing from a low $C_i$ to a higher one the new D will be higher than if 1st order kinetics prevailed.

We have not attempted to interpret the result in terms of precise fractional orders since no steady results leading to such an interpretation ever arose.

(b) Determination of the temperature coefficient.

The usual method of evaluating temperature coefficients is to obtain the steady reaction rate at various temperatures and then to plot the logarithm of the rate constant against the reciprocal of the absolute temperature. The slope of this line being put equal to $- E_A/2.303R$, yields the value $E_A$ which is quoted as the "experimental activation energy".

This value may often be very different from the true surface process activation energy, because of variable heats of adsorption at the different temperatures, and in the method described above $\Delta H$ and $E_A$ cannot be adequately separated. In the special case of a zero order process $E_A = E_{true}$, since the overall rate is not affected by the adsorption which is regarded as complete, and consequently there is no variable $\Delta H$ factor.

The method used to find temperature coefficients or activation energies in this investigation, was to follow the change of initial decomposition at a new temperature after a fast temperature change from a steady decomposition value. By a minor extrapolation to zero time, the decomposition at the two temperatures could be compared, it was assumed, at a constant surface condition and constant $\Delta H$. Since the disturbance of

surface equilibrium is slow, by this method the adsorption on the surface could be considered to be momentarily "frozen", and the temperature coefficient would be equivalent to the activation energy for the surface from which the change was made. A more detailed treatment of this topic will be given in the discussion section.

The temperature coefficient may be calculated in the following way:-

Experiment shows the reaction to be first order with respect to $H_2O_2$ concentration. Hence from (1) above, we have:-

$$k_1 = (2.303/t) \log (1/1-D). \qquad (1)$$

Now, since $k_1 = A \exp. (-E_A/RT)$

or $\ln k_1 = \ln A - E_A/RT$

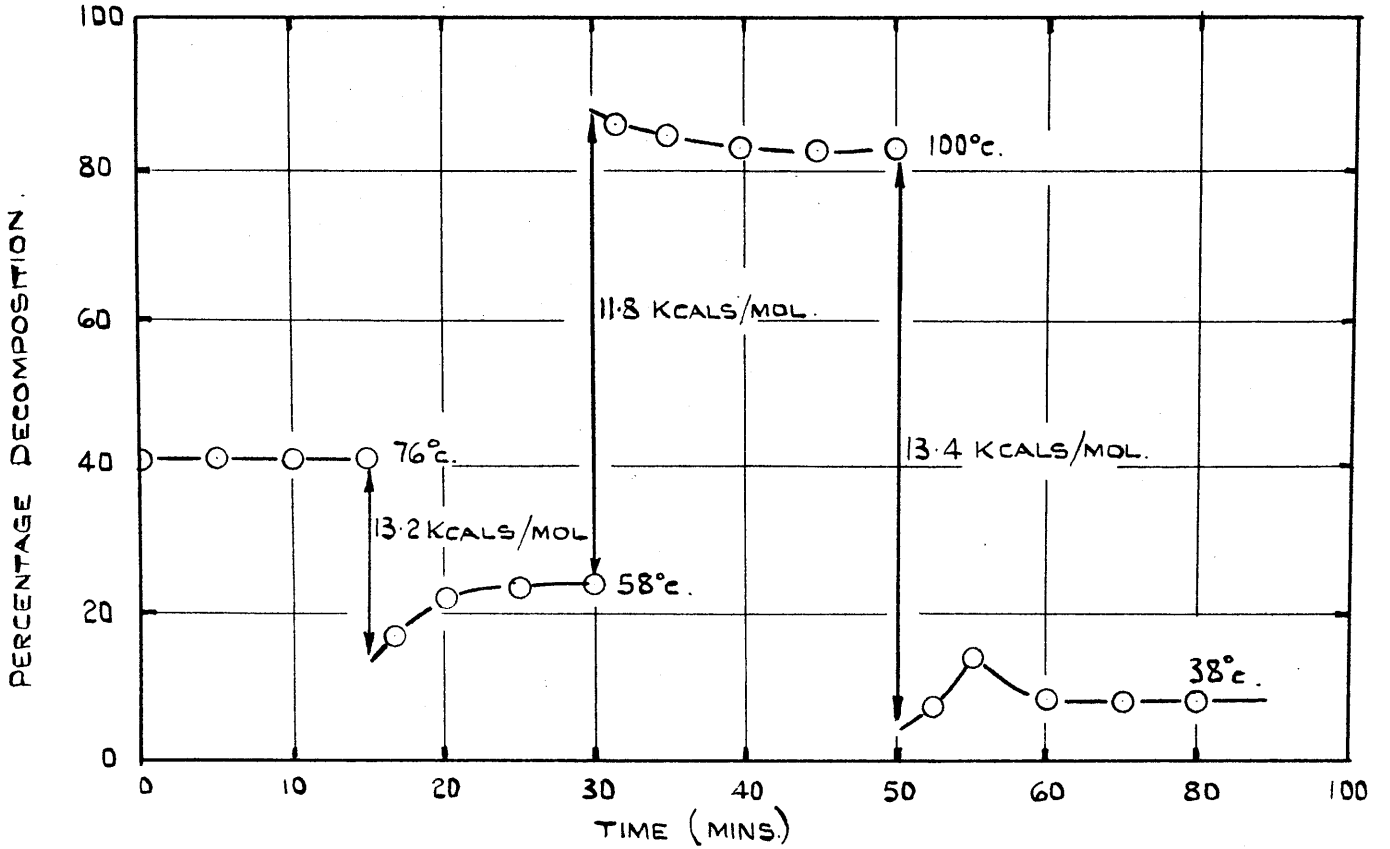
Then, $$\ln k_1 - \ln k_2 = \frac{EA}{R} \cdot \frac{T_1-T_2}{T_1 T_2} \qquad (2)$$

if we may assume A to remain constant during the temperature change. (This will be discussed later but for the moment the assumption may be accpeted for a fast temperature change). Hence by substitution of (1) in (2) we have:-

$$E_A = 4.577. \frac{T_1 T_2}{(T_1-T_2)} \left[ \log. \log \frac{1}{1-D} - \log. \log \frac{1}{1-D_2} \right]$$

which yields the experimental activation energy in terms of decompositions $D_1$ and $D_2$ at temperatures $T_1$ and $T_2$ $^oK$ respectively. Fig. 13 illustrates the general pattern of rate changes found, and the small extrapolation used to find $D_2$ immediately after a temperature change.

The values of activation energy obtained in this fashion were independant of the surface condition of the catalyst. For example, an $Ag/Ag_2O$ plate when prepared as described earlier had an $E_A$ value for




DECOMPOSITION PATTERN, FAST TEMPERATURE CHANGES.
OXIDISED COPPER SLIP CATALYST

FIG. 13.

4.7K.cals/mol between 38-100°C. The same value was found after the plate had been highly etched with H.T.P. solution which gave the catalyst a white, pearly appearance - although the percentage decomposition at the same temperatures was very much different.

(c) Reproducibility with the flow system.

The steady value of the efficiency of a catalyst could usually be duplicated with a similarly but separately prepared sample to within 5% for metals or metal films, and with the bulk oxides to within 1%. The following results demonstrate this. For the metals and metal films the initial behaviour was not quantitatively reproducible but the same trend was always exhibited. On the other hand, bulk oxides gave precise reproducibility in this phase also. The greater spread with oxidised metals may be held to indicate that the metal itself had not been brought into a uniform state before use.

TABLE 2. Illustrating reproducibility of flow measurements with separately prepared samples of the same specimen.

| Oxide Sample | Temperature of Run (°C.) | Time (mins.) from initial exposure of catalyst to $H_2O_2$. | Percentage Decomposition | |
|---|---|---|---|---|
| | | | Sample 1 | Sample 2 |
| $ZnO/Mn_2O_3$ | 60 | 5 | 64.01 | 63.50 |
| " | " | 10 | 56.60 | 56.10 |
| " | " | 15 | 55.50 | 55.20 |
| " | " | 20 | 55.25 | 55.24 |
| " | " | 25 | 55.25 | 55.24 |

TABLE 2 (Continued.)

| Oxide Sample | Temperature of Run (°C.) | Time (mins.) from initial exposure of catalyst to $H_2O_2$. | Percentage Decomposition | |
|---|---|---|---|---|
| | | | Sample 1 | Sample 2 |
| Oxidised "specpure" Fe slip | 100 | 5 | 24.41 | 25.00 |
| " | " | 10 | 20.04 | 36.50 |
| " | " | 15 | 35.52 | 37.25 |
| " | " | 20 | 35.05 | 36.70 |
| " | " | 25 | 35.05 | 36.70 |
| NiO ("green") | 100 | 5 | 65.50 | 56.55 |
| " | " | 10 | 54.00 | 54.50 |
| " | " | 15 | 54.92 | 55.63 |
| " | " | 20 | 54.01 | 54.50 |
| " | " | 25 | 54.01 | 54.50 |

(2) Catalysis on Oxide Films of Pure Metals.

(a) Oxidised flashed metal films. (Nickel and Copper).

Initial changes of efficiency.

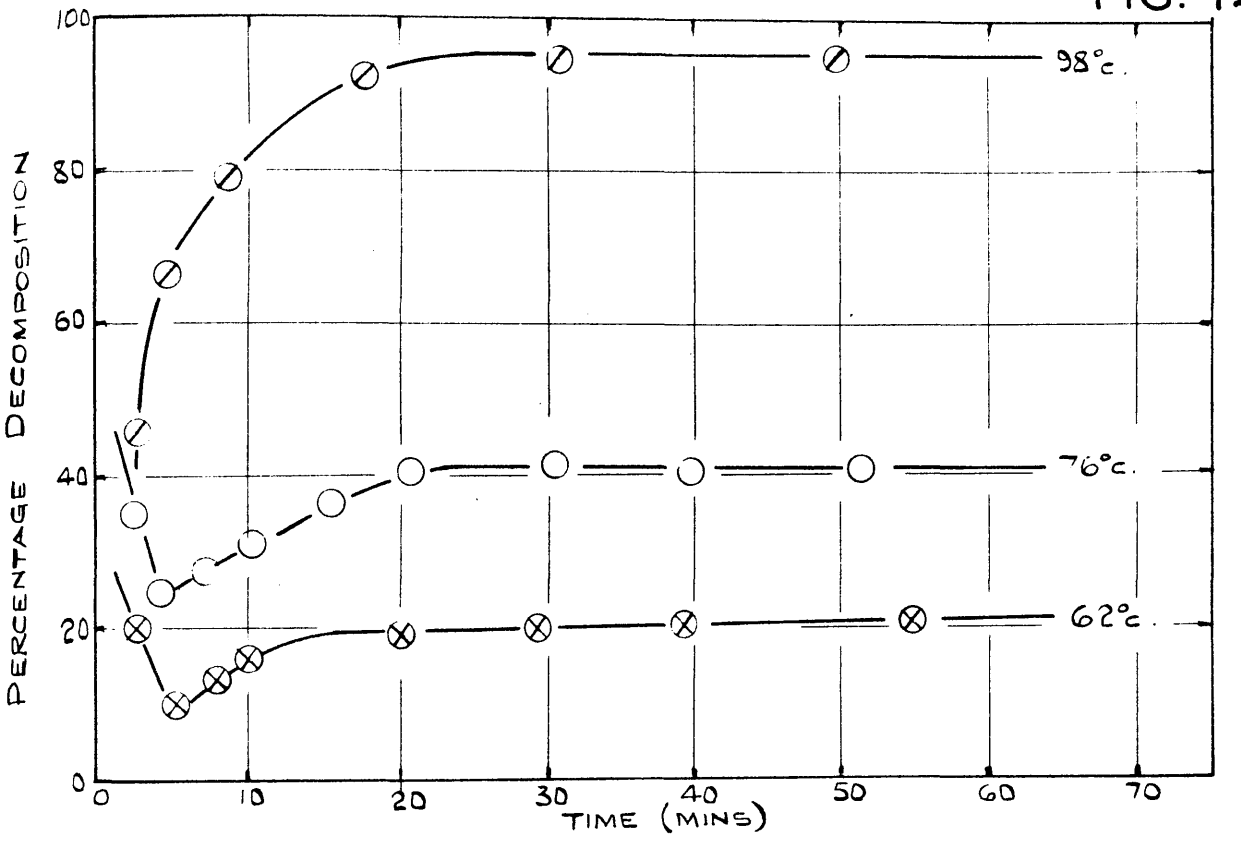
The original object in studying the catalysis on evaporated metal films was twofold. It was intended to compare the catalytic activity of the bulk oxides with that of the same oxide on a pure, clean metal support. Secondly, it was hoped to measure the change of conductivity of the oxide film during catalysis, in the manner used by Gray and Savage (50) and Suhrmann and Schulz (104) to study the adsorption of various gases on metal films. A unit was constructed for this purpose but unfortunately could not be used owing to the pressure of other experimental work.

The kinetics of the decomposition process were examined on copper and nickel films and a detailed investigation carried out on nickel. The films were deposited onto a surface cooled in liquid oxygen. During this process the pressure was kept in the region $10^{-5}$ - $10^{-6}$ mm. Hg., so that there would be negligible contamination of the film surface. Air was then admitted and the films brought quickly to room temperature. After this process the transparent nickel and copper films became black and bronze respectively, due to the uptake of oxygen from the atmosphere. According to Beeck et al. (89) films deposited in this fashion have a roughness factor of approximately 100.

The general pattern of the decomposition changes on the copper films was similar to that found by Hart & McFadyen (81) using $Cu_2O$ covered gauzes (Figs. 14 and 15). The efficiency after a quick drop recovered to a higher steady value, dependant on the temperature of the run. On the other hand,

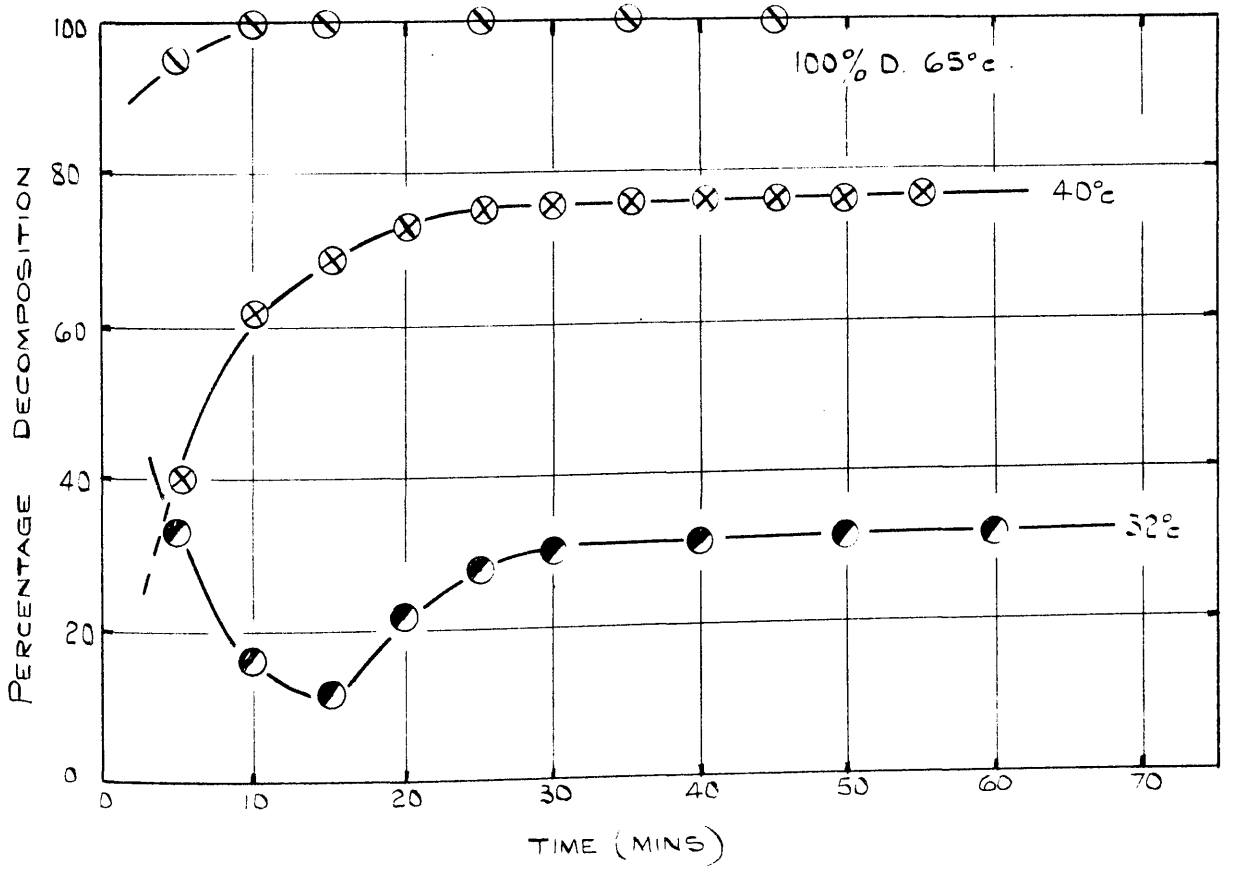
EFFECT OF TEMPERATURE ON ACTIVITY OF COPPER (81)

FIG. 14.




EFFECT OF TEMPERATURE ON ACTIVITY OF OXIDISED COPPER FILM (PRESENT WORK)

FIG. 15.

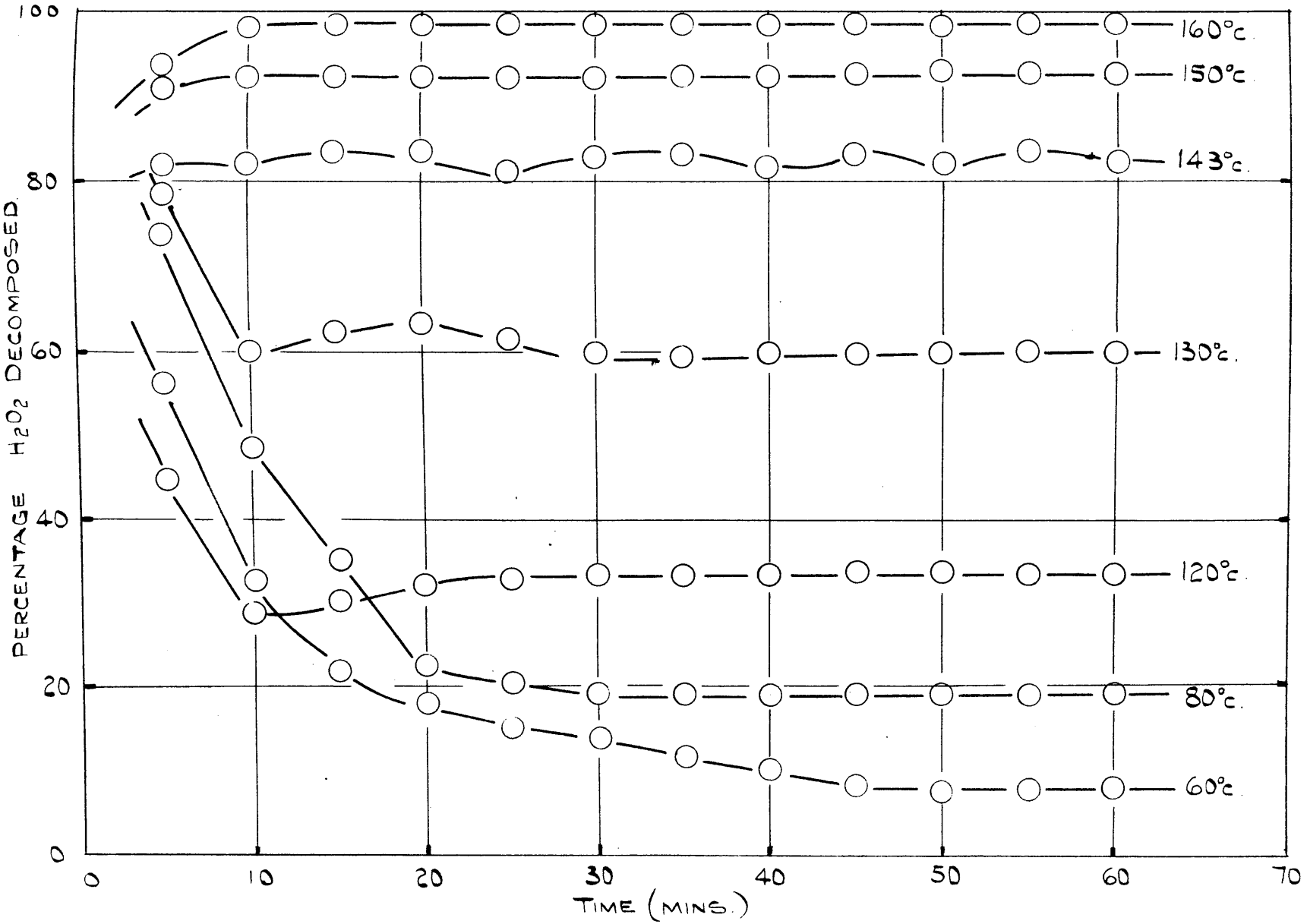


the behaviour of the oxidised nickel films was more complex. Below 140°C, the catalytic efficiency fell exponentially to a steady value in about 30 minutes. At 160°C a fast increase was apparent which steadied to c.100% decomposition after 45 minutes. At intermediate temperatures, cyclic variations occurred which eventually levelled out. This is illustrated in Fig. 16 for a Ni oxidised film 5.7/u thick, and geometric surface area = 31 sq. cm.

Determination of reaction order with films.

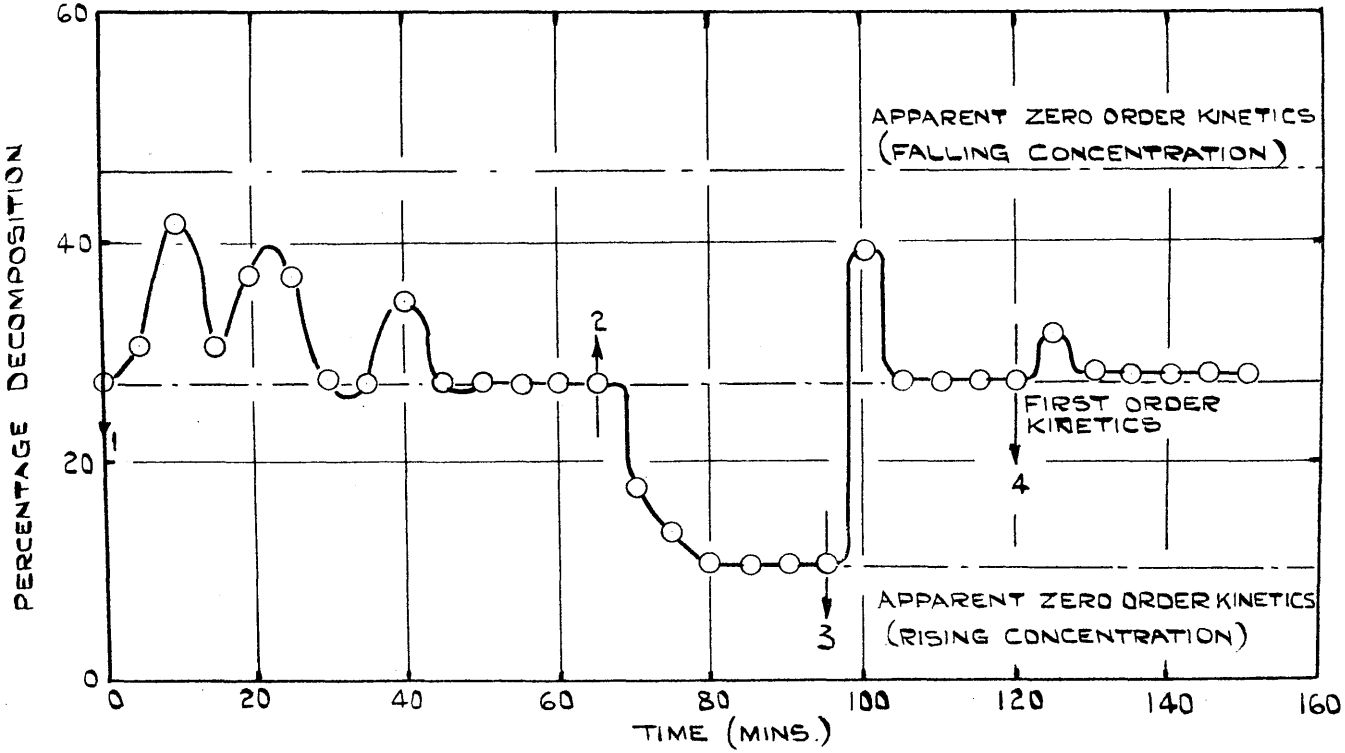
When the steady decomposition value had been reached at a given temperature with a peroxide concentration of 0.88 mm Hg. in the vapour phase; quick changes in concentration were made by reducing the peroxide flow and making up to 300 mls/ minute with dry nitrogen from the alternative stream. Fig. 17 illustrates the behaviour of an NiO film at 100°C in determining the kinetics.

Following a sharp change of $H_2O_2$ concentration to half the original value, (i.e. from $C_i$ to $C_i/2$), the fraction of $H_2O_2$ decomposed remained unchanged for some time. This suggests first order kinetics - the fraction decomposed was, in a given time of contact with the catalyst, independant of the original concentration. Soon, however the amount of catalysis rose rapidly and steadied out briefly to a new higher point before sinking slowly to somewhere near the original amount. This cycle was repeated once or twice before the rate settled at the final value. The upper limit reached on the first cycle when compared with the catalysis before the change to half concentration indicated apparent zero order kinetics, i.e. the total amount of $H_2O_2$ destroyed was independant of the concentration




SHOWING DECOMPOSITION AT VARIOUS TEMPERATURES WITH OXIDISED FLASHED NICKEL FILM (5·7μ THICK).

FIG. 16.




VARIATION OF ACTIVITY OF OXIDISED NICKEL FILM AT 100°C.
FAST CHANGES OF $H_2O_2$ CONCENTRATION.

| | | | | | |
|---|---|---|---|---|---|
| POINT | 1. | :- 0·88 m.m. Hg | → | 0·44 m.m. Hg | $p_{H_2O_2}$ |
| " | 2. | :- 0·44 " " | → | 0·88 " " | " |
| " | 3. | :- 0·88 " " | → | 0·44 " " | " |
| " | 4 | :- 0·44 " " | → | 0·29 " " | " |

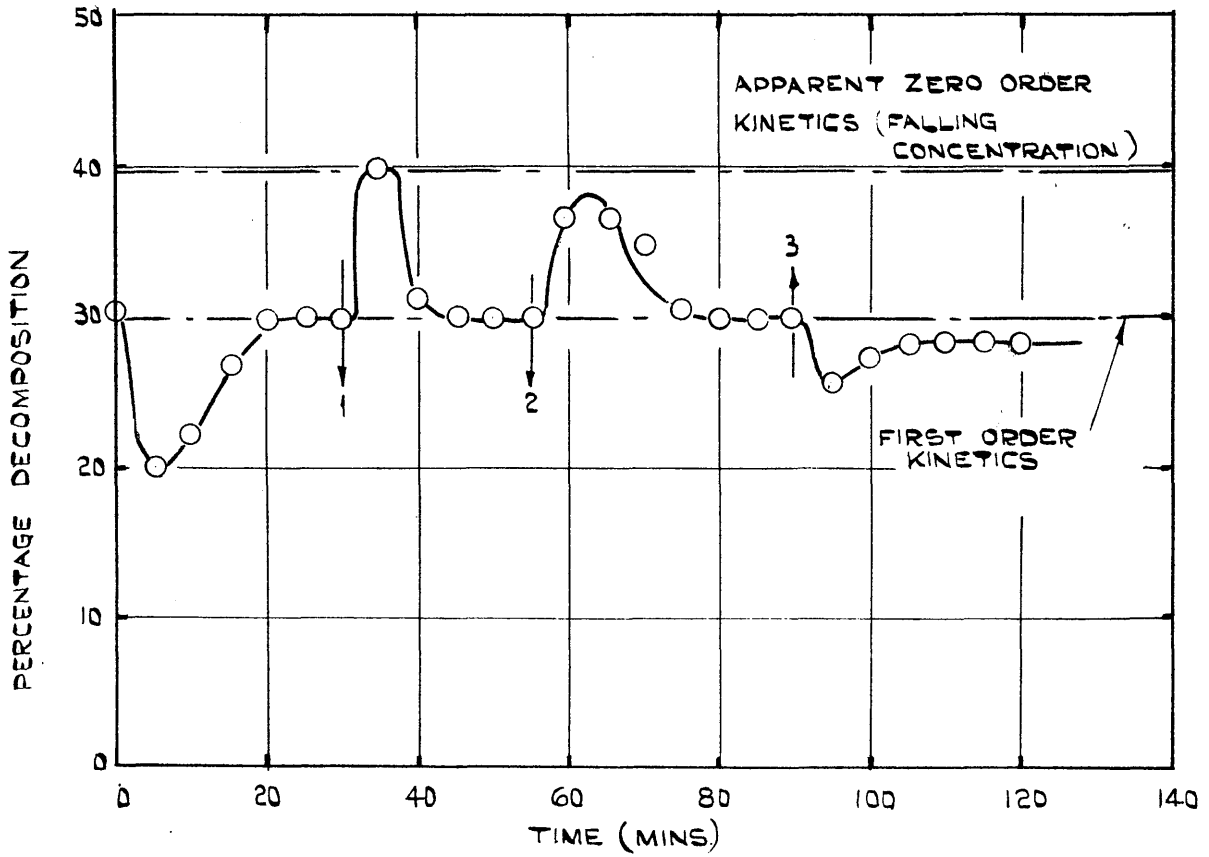
FIG. 17.

reaching the catalyst.

A change back from Ci/2 to Ci gave the reverse of the above. First a rapid movement to a lower decomposition percentage, suggesting again a temporary change which could easily be taken as zero order. This was not allowed to revert to the first order value in the case illustrated. However, on making the change Ci→Ci/2 it remained steady at the original "first order" decomposition, after a minor fluctuation. When the concentration was lowered to Ci/3, a similar though less marked result was recorded.

With the $Cu_2O$ film studied at 38°C, the initial changes were the same as for nickel except that no repetition of the first cyclic variation was observed. After an initial fall in activity at Ci (partial pressure $H_2O_2$ = 0.88 mm Hg.), the catalyst recovered in 15 minutes to a steady decomposition value. Various changes of $H_2O_2$ concentration gave few deviations from a first order process. However, the changes Ci→Ci/2 and Ci/2 →Ci/3 gave a decomposition rise indicating a pseudo zero order process when compared with the steady value at Ci in the first case, and Ci/2 in the second. In 10-20 minutes, these values deteriorated smoothly to the original "first order" decomposition and then remained constant at this value. The final change, Ci/3→Ci, showed a slight efficiency drop which in 15 minutes recovered to a steady level just below the original "first order" decomposition (Fig. 18).

The order of the reaction on nickel films was also examined at 80°C and 140°C and the same variation in kinetic behaviour was observed, i.e. there was always a tendency for the decomposition to rise higher than the first order value in lowering the concentration and to fall lower on raising




DETERMINATION OF REACTION ORDER ON OXIDISED FLASHED COPPER FILM AT 38°C.
CONCENTRATION CHANGES :—

| | | | | |
|---|---|---|---|---|
| POINT | 1 | 0·88 mm Hg | → | 0·44 mm Hg pp $H_2O_2$ |
| " | 2 | 0·44 " " | → | 0·29 " " " |
| " | 3 | 0·29 " " | → | 0·88 " " " |

FIG. 18.

the concentration. Generally, however, these initial fluctuations steadied in time to the original decomposition registered at Ci.

In all the experiments on the metal films the "fast change" kinetics were of the first order. Only temporary fluctuations which were more pronounced with NiO than $Cu_2O$, could lead to the suggestion of a zero order process.

Temperature effect with oxidised flashed films.

The temperature dependance of the reaction rate with NiO was examined in the region 60-160°C, with a partial pressure of 0.88 mm Hg. of $H_2O_2$. The kinetics were taken as first order right through the temperature range. Table 3 below gives the results obtained for the temperature coefficient in a detailed examination of a fully oxidised nickel film 5.7/u thick.

TABLE 3. Experimental activation energies, oxidised nickel film 5.7/u thick. (p.p. $H_2O_2$ = 0.88 mm Hg.)

| Temperature Change (°K) | | Decomposition Change (%) | | Activation Energy (K.cals/mol.) |
|---|---|---|---|---|
| $T_1$ | $T_2$ | $D_1$ | $D_2$ | |
| 433 | 423 | 99 | 92 | 22.0 |
| 423 | 416 | 92 | 82 | 19.3 |
| 416 | 403 | 82 | 59 | 17.4 |
| 333 | 353 | 7 | 17 | 11.3 |
| 353 | 373 | 17 | 28 | 10.9 |

Above 120°C the stepwise temperature changes yield activation energies in the region 17-22K,cals/mol. In the range 60-100°C the temperature

coefficient indicates an apparent activation energy of 11 K.cals/mol.

Similar results were obtained with the other oxidised nickel films as shown in Table 4 for the temperature changes, 60-100°C and 120-160°C.

TABLE 4. Experimental activation energies, oxidised nickel films.

(p.p. $H_2O_2$ = 0.88 mm. Hg).

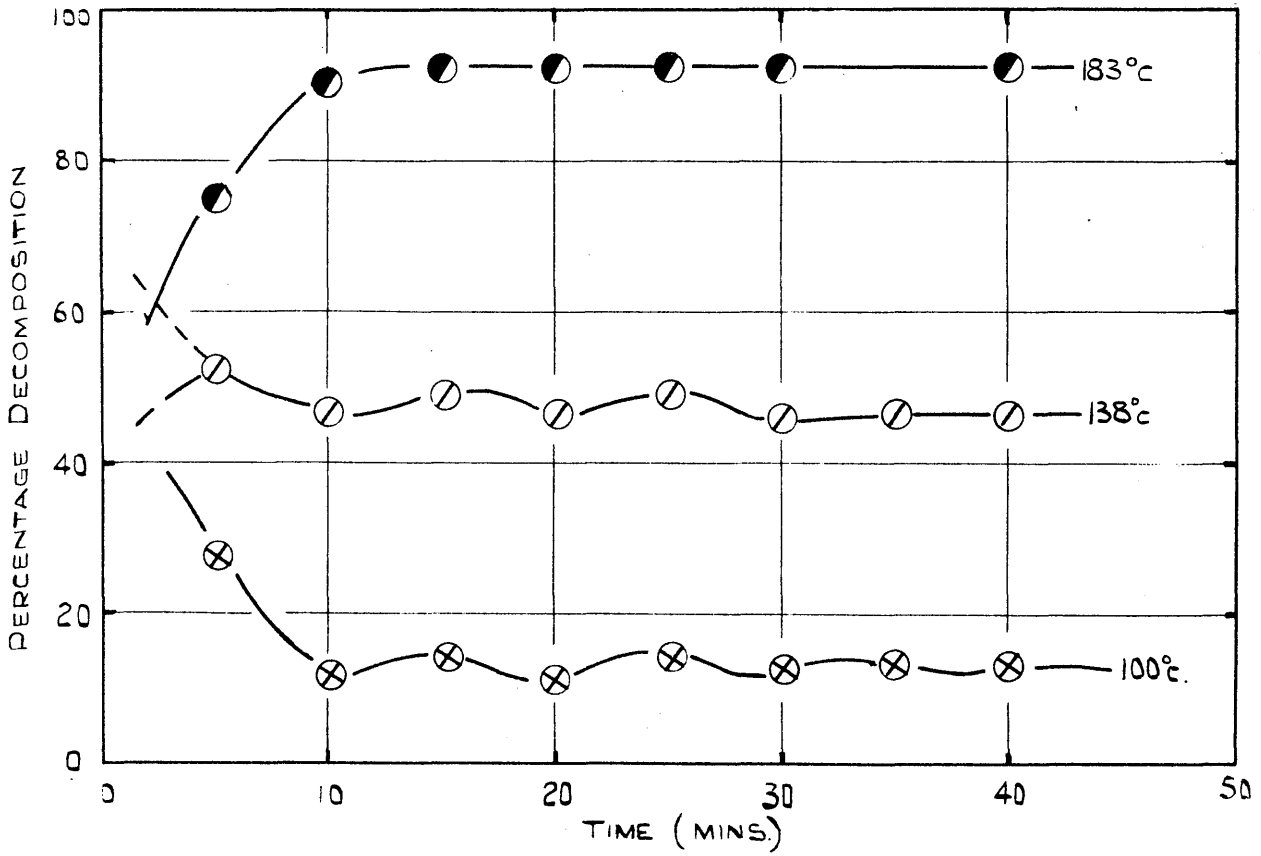
| Oxide Film | Thickness (/u) | Activation Energy. K.cals/mol.) | |
|---|---|---|---|
| | | 60 - 100°C | 120 - 160°C. |
| NiO | 7.22 | 11.2 | 20.3 |
| NiO | 9.25 | 11.4 | 22.9 |
| NiO | 11.24 | 11.0 | 20.2 |
| $Cu_2O$ | 7.63 | 12-14 | - |

The value obtained with the $Cu_2O$ film, which was of the same order as that found by Hart and McFadyen (81) with $Cu_2O$ covered metal gauzes, was determined between 38-60°C, since the high activity prohibited determinations above 65°C where 100% decomposition was recorded.

The values for the activation energy of the various NiO films can be seen from Table 4 to be relatively unaffected by small differences in film thickness.

Surface areas of films.

Attempts to measure the surface areas of the films by the B.E.T. method, using as adsorbent $C_2H_4$ at 183°C, were unsuccessful. A better method has been demonstrated by Rideal and Trapnell (105). It involves oxygen chemisorption, and the authors found that the surface areas of their films were directly proportional to the weight. However as no comparative




EFFECT OF TEMPERATURE ON ACTIVITY OF "SPECPURE" NICKEL SLIP SHOWING INITIAL CHANGES.

FIG 19.

studies were made with the flashed films, the surface area determinations were not pursued.

(b) Oxidised metal slips.

The metals examined were cut to fit the flow reactor in Fig. 4. The methods of preparation and cleaning have been detailed under the section on materials.

It is proposed here to deal with NiO/Ni first, as nickel oxide was taken as the model in all the experiments, including the bulk oxide and impurity addition studies.

(i) Nickel/nickel oxide.

Initial activity changes and reaction order.

The course of the changes of the catalytic efficiency on first exposure to $H_2O_2$ of the oxidised "specpure" nickel slips was similar to that of the nickel films. The same cyclic changes of efficiency were observed at c.100°C and also similar fluctuations on changing the $H_2O_2$ concentration.

Fig. 19 illustrates the changes of efficiency of the catalyst before reaching the steady decomposition level at various temperatures. Figs. 20(a) and 20(b) show the variations found with the reaction order at 138°C and 183°C respectively, with varying $H_2O_2$ concentrations.

Fig. 20(a) shows the temporary increase in efficiency of an Ni/NiO "Specpure" slip on making fast concentration changes at 138°C. The first change at point (1) gave a slight activity drop on doubling the original $H_2O_2$ concentration. Following this, when the steady value had been attained, a change back to Ci gave an increase of activity which in 10 minutes fell to the original "first order" decomposition; and remained at

SHOWING TEMPORARY INCREASE OF EFFICIENCY
ON DECREASING $H_2O_2$ CONCENTRATION "SPECPURE"
Ni AT 138°C. POINT 1 :- 0·44 mm. → 0·88 mm Hg pp $H_2O_2$
2 :- 0·88 mm. → 0·44 " " "
3 :- 0·44 mm. → 0·29 " " "

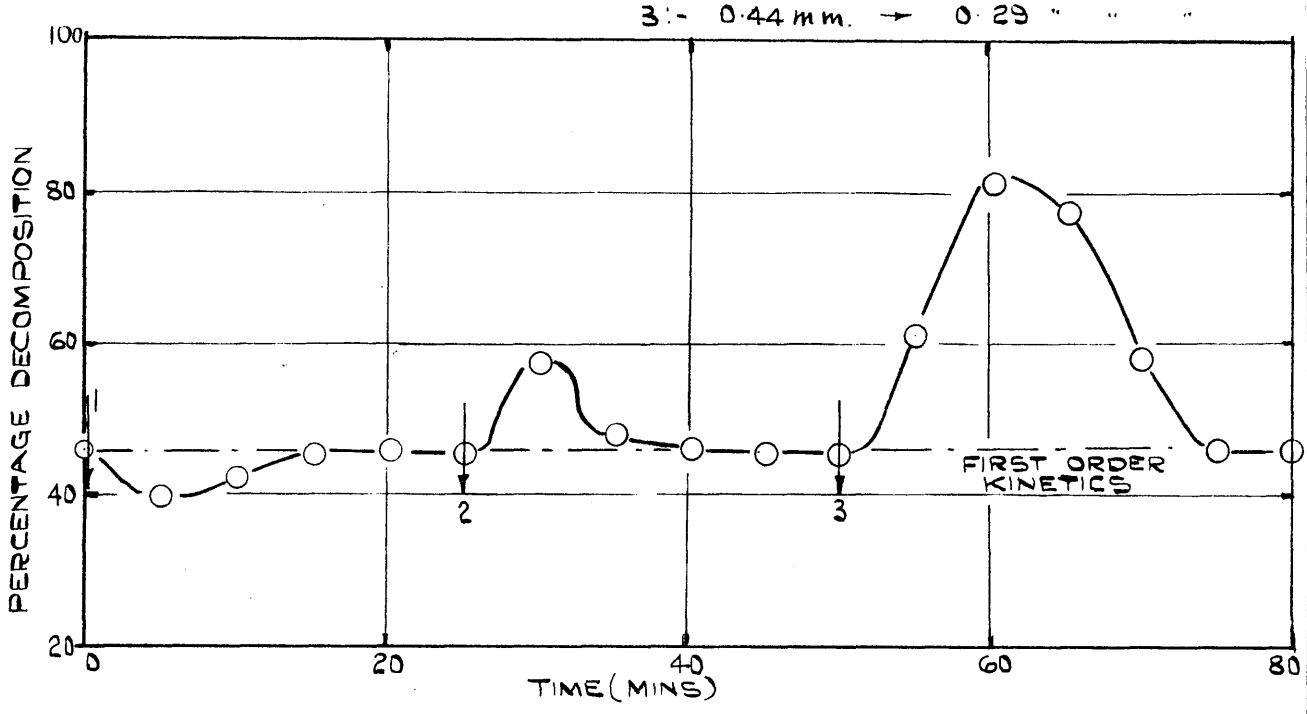



FIG. 20.A.

SHOWING APPARENT DEACTIVATION ON
INCREASING $H_2O_2$ CONCENTRATION "SPECPURE" Ni AT 183°C.

POINT 1 :- 0·88 mm → 0·44 mm. Hg pp $H_2O_2$
2 :- 0·44 " → 0·29 " " "
3 :- 0·29 " → 0·44 " " "

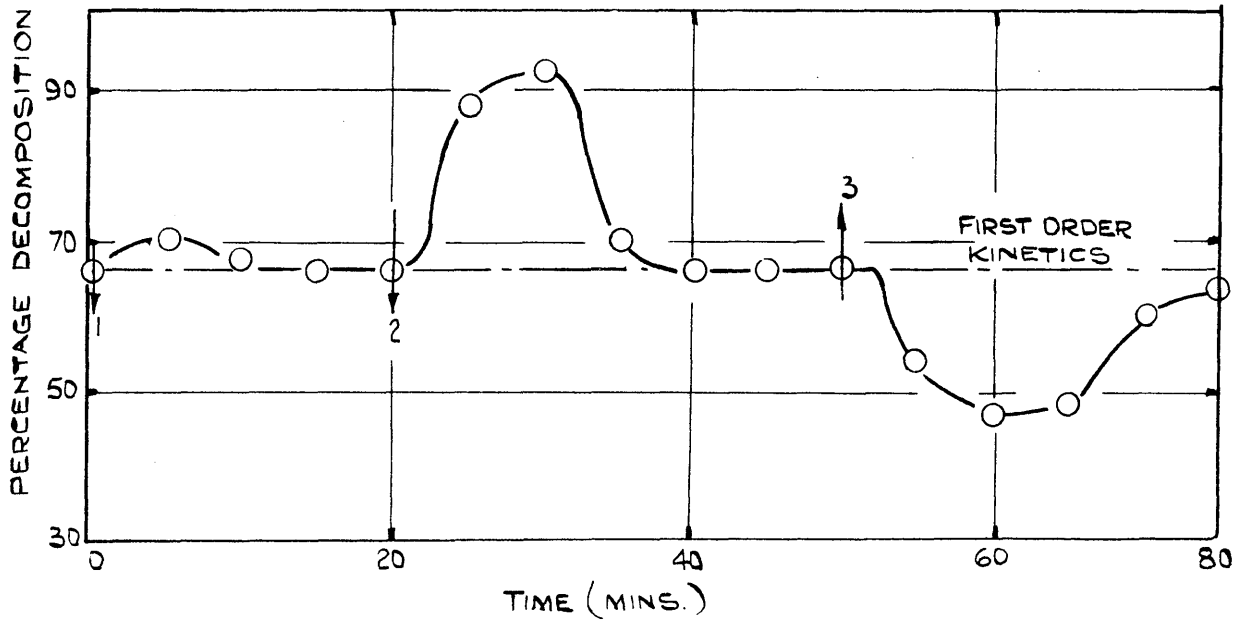



FIG. 20B.

this value, after a temporary increase in efficiency lasting 25 minutes, on dropping the concentration to 2 Ci/3.

The apparent deactivation of an Ni/NiO catalyst in runs of increasing $H_2O_2$ concentration at 183°C is illustrated in Fig.20(b). The changes Ci $\longrightarrow$ Ci/2 $\longrightarrow$ Ci/3 were accompanied by an initial efficiency increase, exactly analogous to those recorded at 138°C. After the catalyst had reached a steady value at Ci/3, the reverse change to Ci/2 was accompanied by a fast efficiency drop which after 25 minutes began to level out and approach the original "first order" decomposition from below.

In all the experiments the departure from ideal first order kinetics was slight over the whole process. Again, however, like the Ni/NiO films there was an initial tendency for the catalyst to "activate" on lowering the concentration of peroxide vapour, and to "poison" on raising the concentration. In this instance also, unlike the oxidised flashed nickel films, initial cyclic variations of efficiency on making the concentration changes were not apparent.

Temperature coefficient.

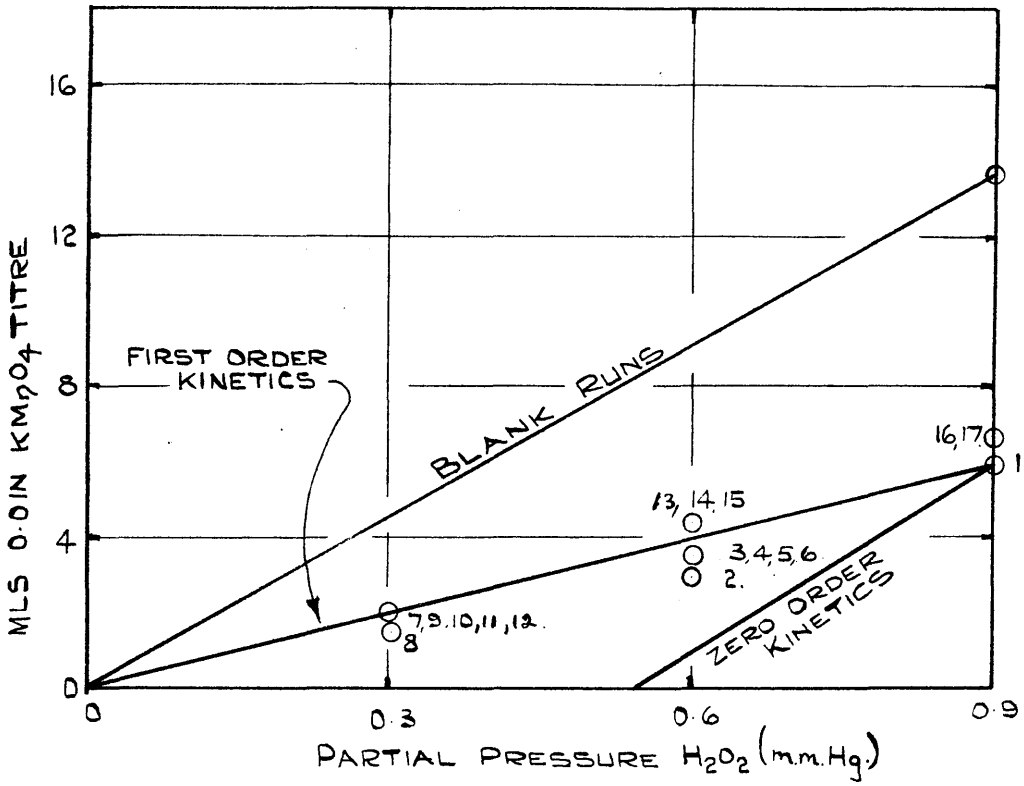
The temperature coefficient of the decomposition on the oxidised metal slips was found by making fast temperature changes in the sequence:- 100°C $\longrightarrow$ 138°C $\longrightarrow$ 183°C $\longrightarrow$ 100°C. In all cases the initial changes of the decomposition at the new temperature were carefully measured to enable the evaluation of the rate change by extrapolation to zero time.
Table 5 below gives the values found with an $H_2O_2$ partial pressure of 0.96 mm Hg. at a constant flow rate of 300 mls/min.

TABLE 5. Temperature coefficient nickel/nickel oxide; fast temperature changes.

| Temperature Change (°K). | | Decomposition at $T_1$ (%) | | Decomposition at $T_2$ (%) | | | Activation Energy (K.cals/mol.) |
|---|---|---|---|---|---|---|---|
| $T_1$ | $T_2$ | Initial Value | Steady Value | Initial Value | Extra-polated Value | Steady Value | |
| 373 | 411 | 11.2 | 8.0 | 52.1 | 54.0 | 46.4 | 11.7 |
| 411 | 456 | 52.1 | 46.4 | 93.6 | 95.3 | 90.1 | 13.3 |
| 456 | 373 | 93.6 | 90.1 | 7.5 | 5.2 | 9.1 | 15.7 |
| 373 | 456 | 27.5 | 12.2 | 87.5 | 90.0 | 86.1 | 11.8 |
| 456 | 373 | 87.5 | 86.1 | 5.6 | 4.1 | 6.9 | 16.1 |

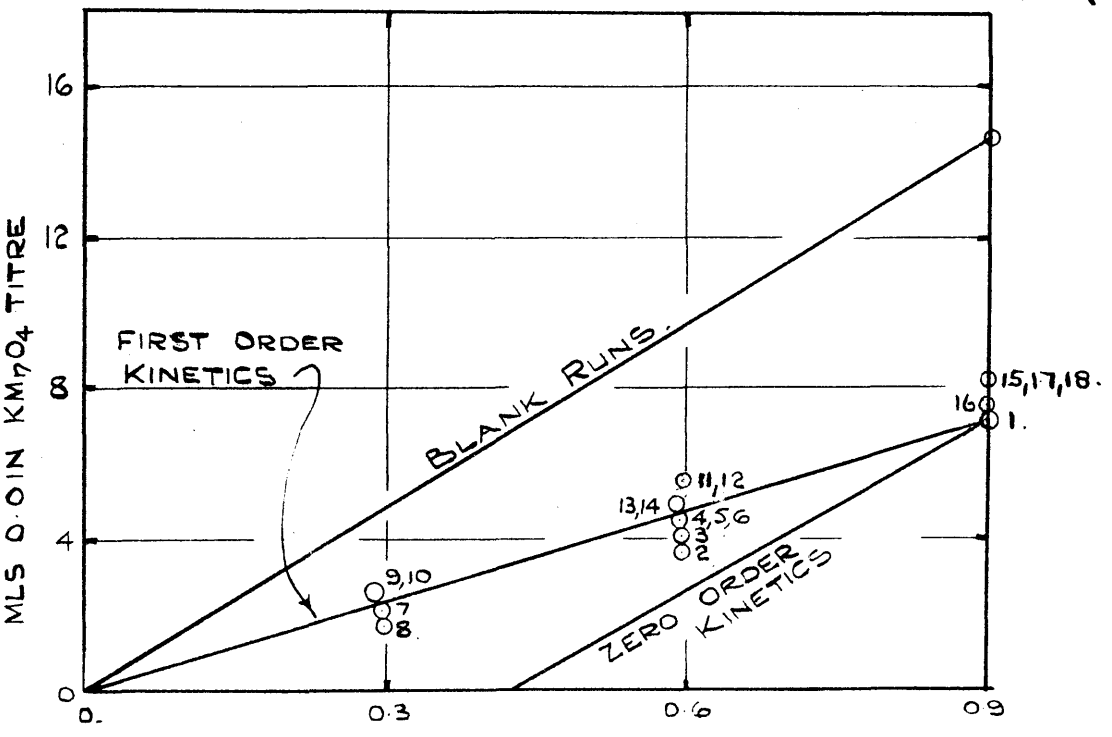
The first three values in the table refer to figures obtained in the course of a single run on one sample of catalyst. The last two figures refer to a fresh slip, which took 40 minutes to settle at 12.2% decomposition at 100°C. When this had remained steady for a further 20 minutes, a rapid temperature change to 183°C was effected and the steady value attained in 15 minutes. Similarly after the drop to 100°C, the decomposition value became constant in 15 minutes at 6.9%

The table shows that the surface prepared at 183°C was associated with a higher energy of activation than the surfaces prepared at the lower temperatures, (138°C, 100°C). This effect was similar to that described with the NiO films and although the actual figures are not strictly comparable because of the different methods of surface preparation; they are in very good agreement especially at the lower temperatures. Temperature changes were made less quickly in the flashed film determinations.



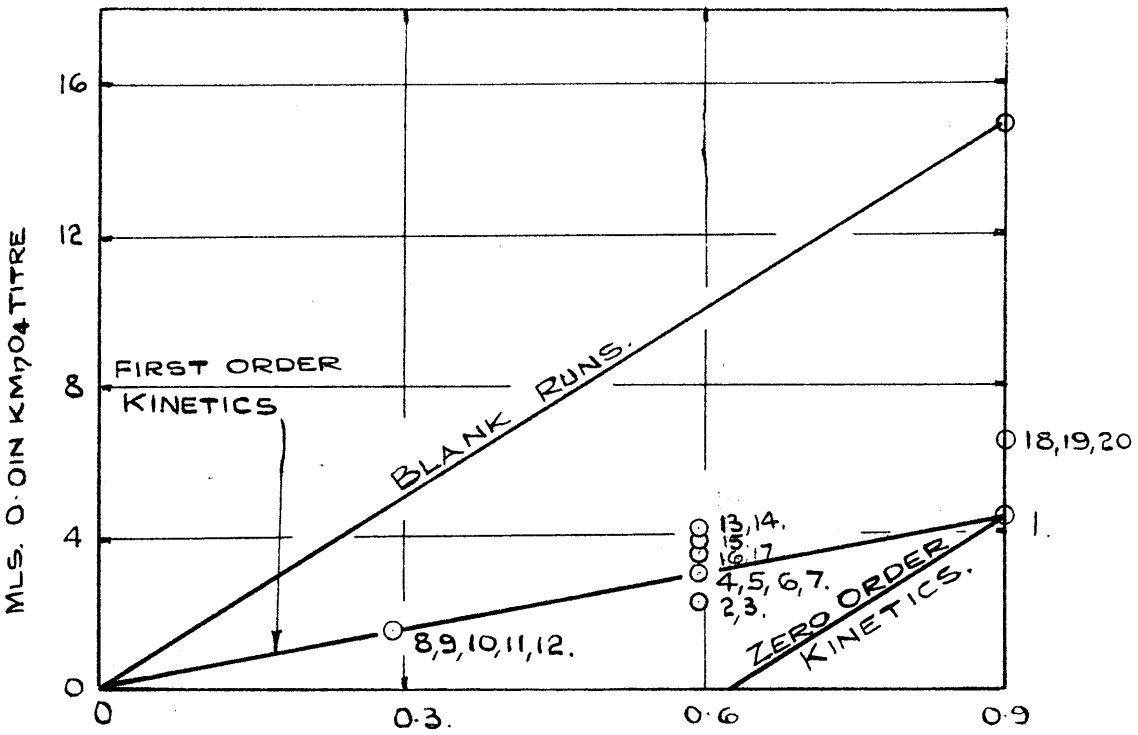

DECOMPOSITION KINETICS. COBALT SLIP AT 78°C.
POINTS NUMBERED AT 5 MINUTE INTERVALS.

FIG. 21(a)



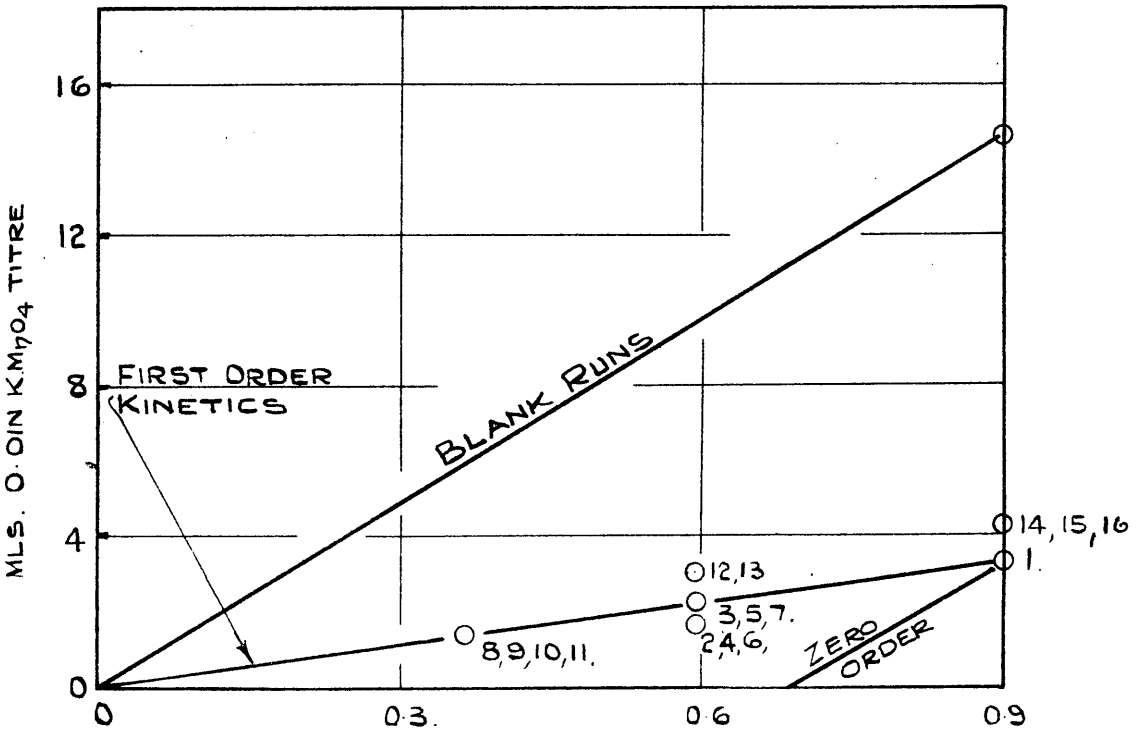

DECOMPOSITION KINETICS. COPPER SLIP AT 78°C.

FIG. 21(b)




DECOMPOSITION KINETICS, SILVER SLIP AT 60°C.
POINTS AT 5 MINUTE INTERVALS.

FIG. 21(c.)




DECOMPOSITION KINETICS,
MANGANESE SLIP AT 60°c.

FIG. 21(d.)

Other metal/metal oxides.

The other metals examined in slip form fall into three classes:-

(1) Cu, Ag, Co, Mn - Active Catalysts.

(2) Fe, Zn - Intermediate in Activity.

(3) Al, Sn - Inactive Catalysts.

All the metals used would bear a protective film of oxide as shown by the work of Mott (38) and Rhodin (94, 106), as already described in the section on materials. It is proposed to deal with each group separately.

(ii) Class (1).

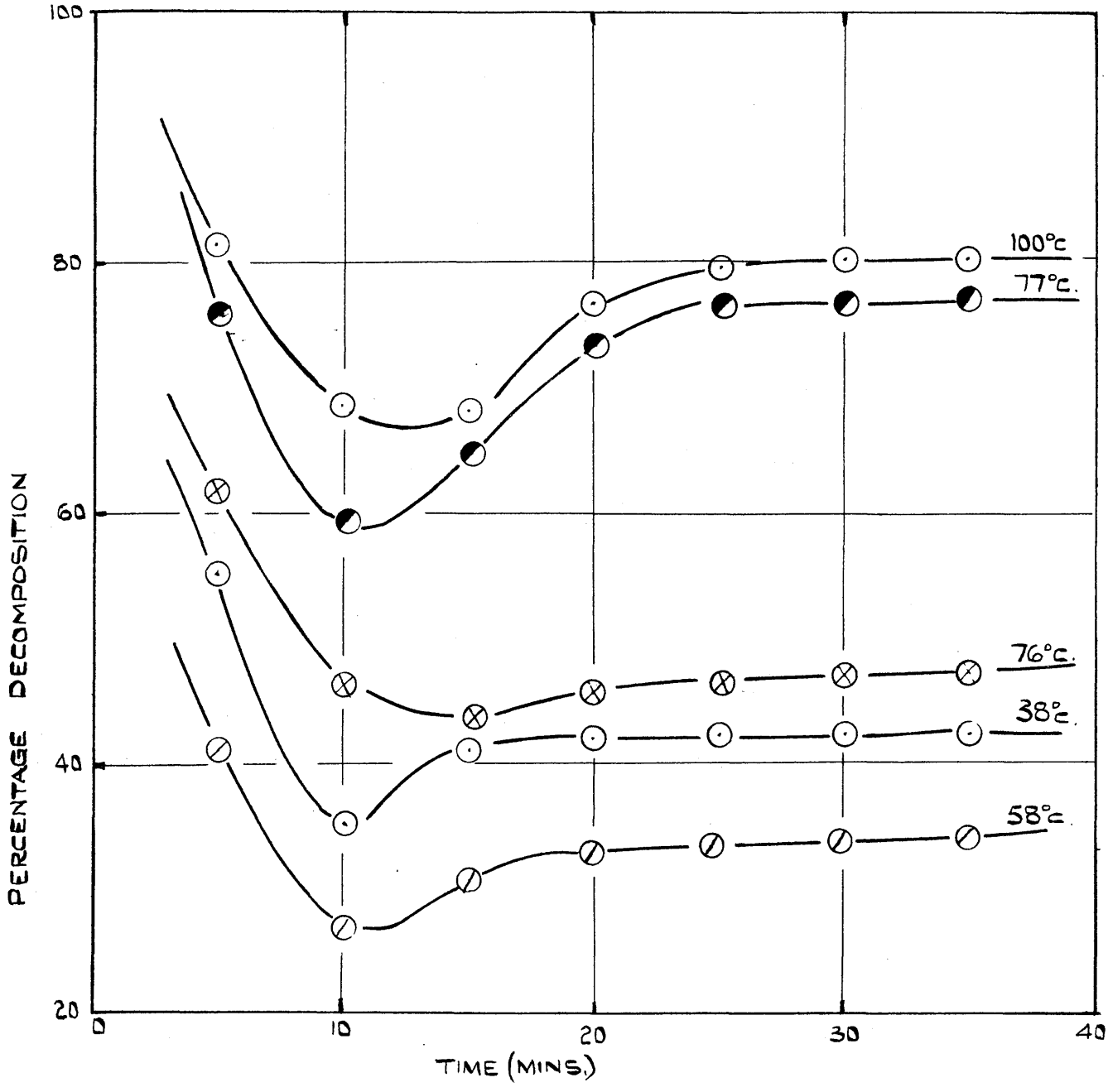
The metals in this class all form stable, coherent oxide films of lower oxides with a slight tendency to pass to a higher valency state at the surface.

Kinetic order of decomposition.

The kinetics of the decomposition on these surfaces showed much less departure from first order behaviour on making changes of concentration, than Ni/NiO. There was, however, a slight tendency, exhibited by all the specimens, towards deactivation in making a change Ci/3 $\rightarrow$ 2Ci/3 $\rightarrow$ Ci. Figs. 21(a), (b), (c), (d) show the determination of reaction order on the four materials at 78°C or 60°C. The points are numbered in experimental sequence at 5 minute intervals, point (1) represents the steady decomposition value at Ci (300 mls/min. through $H_2O_2$ saturator; $H_2O_2$ partial pressure = 0.88 mm Hg) after the initial fluctuations had settled.

Initial activity changes.

The initial efficiency changes on first exposure of these catalysts to $H_2O_2$ vapour are shown in Fig. 22. The general pattern of the decom-




INITIAL ACTIVITY VARIATIONS CLASS (1.)

METAL/METAL OXIDES

⊙ Mn/MnO; ⊘ $Ag/Ag_2O$; ◐ Co/CoO; ⊗ $Cu/Cu_2O$.

FIG. 22.

position was similar with all of the specimens on which a fast efficiency drop quickly recovered to a steady value in 20-25 minutes depending on the temperature of the run. The higher temperatures generally accelerating the attainment of the steady decomposition value.

Temperature coefficient.

The activation energies obtained from the temperature coefficients in the range 38 - 100°C are summarised in Table 6 below.

TABLE 6. Experimental activation energies for class (1) metal/metal oxides. Fast temperature changes 38-100°C. Partial pressure $H_2O_2$ = 0.88 mm Hg.

| Metal | Probable Surface Oxide | Temperature Change (°C) | | Decomposition Change (%) | | Activation Energy (K.cals/mol.) |
|---|---|---|---|---|---|---|
| Co (1) | CoO | 77 | 60 | 78.0 | 40.0 | 14.5 |
| | | 60 | 100 | 50.0 | 90.0 | 12.3 |
| Co (2) | CoO | 77 | 60 | 72.5 | 35.0 | 14.7 |
| | | 60 | 100 | 50.0 | 90.0 | 12.3 |
| Cu | $Cu_2O$ | 80 | 58 | 40.0 | 10.0 | 13.2 |
| | | 58 | 100 | 24.0 | 87.5 | 11.8 |
| | | 100 | 38 | 84.0 | 5.0 | 13.4 |
| Mn* | Mn O | 77 | 59 | 64.0 | 47.5 | 4.0 |
| | | 59 | 100 | 60.0 | 84.0 | 4.1 |
| | | 100 | 38 | 83.0 | 42.5 | 4.7 |
| Ag | $Ag_2O$ | 38 | 100 | 19.5 | 51.0 | 4.7 |
| | | 100 | 38 | 49.5 | 17.0 | 4.9 |
| | | 38 | 100 | 49.0 | 86.5 | 4.6** |

* Contained 8% copper.

** Etched.

It should be noted that the temperature change from 100-38°C, could not be accomplished with cobalt because at 100°C the decomposition was 100% with this oxide.

Again, it is evident that the surface prepared at the higher temperatures is associated with a higher activation energy than that prepared at 38°C. As can be seen from the figures with two separate cobalt plates, the values are highly reproducible.

It is also interesting to note that whilst highly etching the surface of the $Ag/Ag_2O$ plate gave a decomposition of peroxide vapour at 38°C which formerly was registered at 100°C; no appreciable alteration was apparent in the temperature coefficient.

(iii) Class (2).

The metals examined in this class were Fe and Zn, giving rise to surface oxides ZnO and in the case of iron $FeO/Fe_2O_3$ as has been shown by Nelson (93) for treatment in air below 200°C.

Catalytic efficiency and kinetic order of decomposition.

These metal/metal oxides were less active than those of class (1). No decomposition was observed below 78°C and the kinetics were therefore examined in the temperature range 100-183°C. The initial exponential decay which was observed with the active oxides was not apparent in these cases. In fact, steady catalysis was reached almost immediately, or, at the most, 5 minutes from the beginning of the reaction. However, with Zn/ZnO, but not with $Fe/FeO/Fe_2O_3$, a slow poisoning of the surface was observed so that, for example, at 138°C in 2 hours the decomposition fell

from 55% to zero. This slow deactivation was much accelerated in the process of order determination on Zn/ZnO and, in fact, became equally marked under these conditions for the iron surface.

On reducing the initial concentration, $C_i$, a fairly constant efficiency was obtained, but an increasing value from Ci/3 to Ci/2 or $C_i$ showed a sudden complete poisoning of the surface with both oxides. Tables 7 and 8 illustrate this phenomena for iron and zinc respectively.

TABLE 7. Showing deactivation of iron/iron oxide in concentration changes (100°C). Samples taken every five minutes.

| $H_2O_2$ concentration (mm. Hg.) | Percentage Decomposition | Time from start of run (mins.) | Remarks |
|---|---|---|---|
| 0.98 | 34.4 | 5 | |
| 0.98 | 34.5 | 10 | |
| 0.98 | 34.5 | 65 | ) |
| 0.65 | 35.0 | 70 | ) First order kinetics |
| 0.65 | 34.7 | 75 | |
| 0.65 | 34.6 | 110 | ) |
| 0.33 | 34.6 | 115 | ) First order kinetics |
| 0.33 | 34.7 | 120 | |
| 0.33 | 34.7 | 135 | |
| 0.65 | 14.9 | 140 | Deactivation |
| 0.65 | <2.0 | 145 | " |
| 0.33 | 0.0 | 150 | Poisoned |
| 0.65 | 0.0 | 155 | " |
| 0.98 | 0.0 | 160 | " |

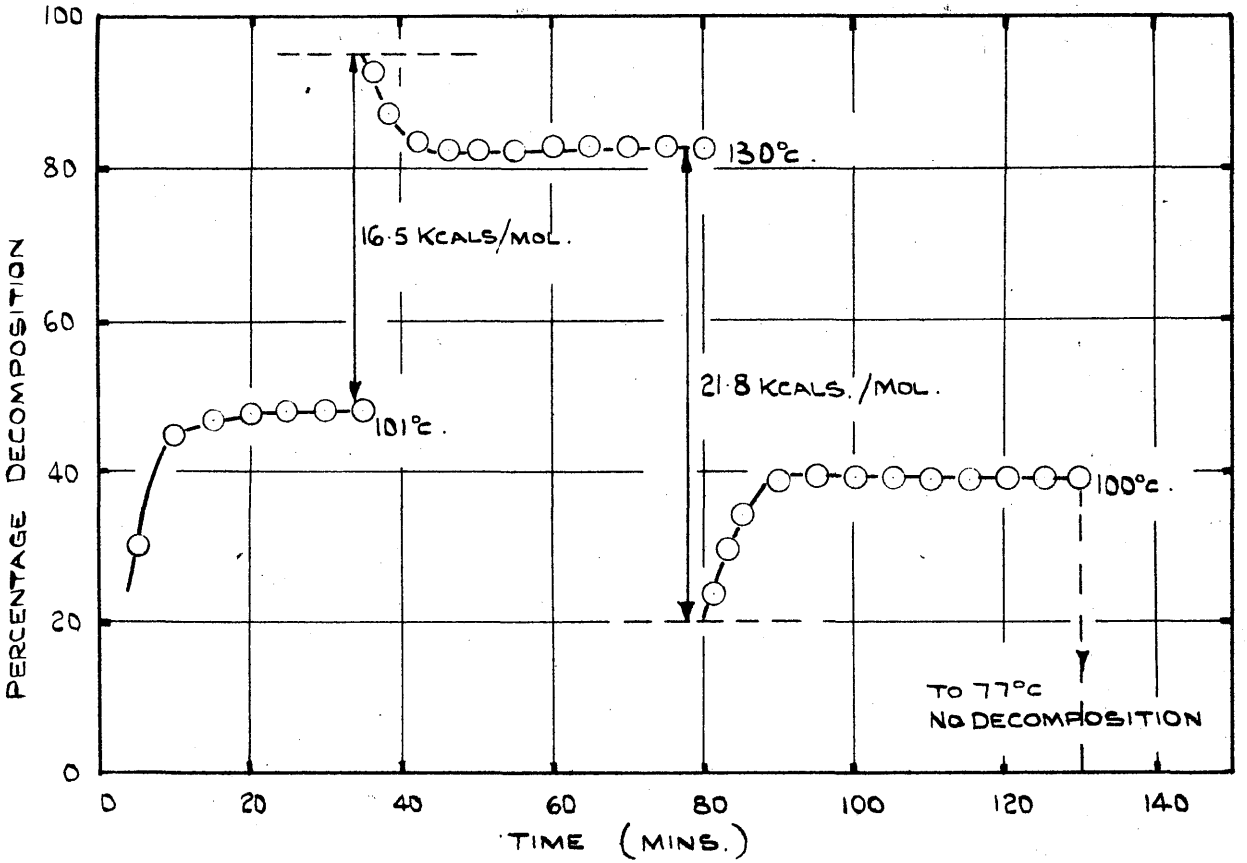
TABLE 7 Continued, T = 138°C.

| $H_2O_2$ concentration (mm. Hg) | Percentage Decomposition | Time from start of runs (min.) | Remarks |
|---|---|---|---|
| 0.98 | 77.5 | 5 | |
| 0.98 | 78.0 | 30 | First order kinetics |
| 0.65 | 78.6 | 35 | |
| 0.65 | 78.3 | 40 | |
| 0.65 | 78.1 | 65 | First order kinetics |
| 0.33 | 78.4 | 70 | |
| 0.33 | 78.2 | 95 | |
| 0.65 | 51.0 | 100 | Deactivation. |
| 0.65 | 27.4 | 105 | " |
| 0.65 | 12.9 | 110 | " |
| 0.65 | 3.7 | 115 | " |
| 0.98 | 0.0 | 120 | Poisoned |
| 0.98 | 0.0 | 135 | " |

It can be seen from the above table that whenever the surface becomes inactive at a given concentration it remains so at a change to a higher or lower concentration. It seems to be permanently poisoned. The iron slips did not show the initial activity variations on lowering the concentration that was displayed by the class (1) metal/metal oxides. Indeed, in these experiments the steady decomposition was reached almost immediately on making a change.

TABLE 8. Showing deactivation of Zn/ZnO slip in concentration changes ($100^{o}C$). Five minute samples.

| $H_2O_2$ concentration (mm. Hg) | Percentage Decomposition | Time from start of run (mins.) | Remarks |
|---|---|---|---|
| 0.98 | 27.3 | 5 | |
| 0.98 | 27.2 | 10 | |
| 0.65 | 23.0 | 15 | |
| 0.65 | 20.0 | 20 | |
| 0.33 | 15.9 | 25 | Steady |
| 0.33 | 9.7 | 35 | Deactivation. |
| 0.65 | 3.1 | 40 | |
| 0.65 | 0.0 | 45 | Poisoning |
| 0.98 | 0.0 | 50 | " |
| 0.98 | 25.9 | Overnight | |
| 0.98 | 25.3 | 10 | |
| 0.65 | 19.7 | 15 | |
| 0.65 | 17.2 | 20 | Steady |
| 0.65 | 16.9 | 25 | Deactivation. |
| 0.33 | 14.0 | 30 | |
| 0.33 | (<2.0) | 35 | Poisoning |
| 0.65 | 0.0 | 40 | " |
| 0.65 | 0.0 | 50 | " |




EFFECT OF RAPID TEMPERATURE CHANGES ON OXIDISED "SPECPURE" IRON SLIP. SHOWING MINOR EXTRAPOLATION TO "ZERO" TIME

FIG. 23.

Table 8 indicates that zinc/zinc oxide deactivates on lowering the concentration to 2Ci/3, and the surface is more readily poisoned than iron (which at a steady $H_2O_2$ concentration does not tend to lose activity). It can be seen that the zinc catalyst recovered to a similar activity when left overnight in the reaction tube, but quickly "poisoned" again in a new run when exposed to $H_2O_2$ vapour.

The steady deactivation was too fast to permit satisfactory order determinations with zinc but if the rate deterioration is allowed for, approximately first order kinetics are found.

Temperature coefficient.

The temperature coefficient of the reaction rate on iron/iron oxide was found to be in the region 16-20K.cals/mol for the temperature changes shown in Fig. 23. For zinc/zinc oxide an estimate was made on the assumption of the reaction being first order:-

TABLE 9. Results of quick temperature changes on Zn/ZnO.

($p.p.H_2O_2$ = 0.88 mm. Hg.) Freshly prepared sample.

| Temperature Change (°C) | | Decomposition Change (%) | | Activation Energy (K cals/mol) |
|---|---|---|---|---|
| 100 | 78 | 26 | 3 | 33.9 |
| 78 | 100 | 3 | 25 | 33.5 |

(iv) Class (3) - Catalytic activity and kinetic order of decomposition.

The two metal/metal oxides, based on aluminium and tin, in this class were found to be even less active than zinc/zinc oxide. Detectable activity towards $H_2O_2$ vapour was only displayed at temperatures above 140°C. Aluminium, which had been exposed to the air for several days, gave no

decomposition at 140°C and less than 2% at 183°C. After treating this surface in a flowing atmosphere of hydrogen at 500°C for several hours, (with the object of activating the surface), quickly cooling and transferring to the flow apparatus; steady decompositions were obtained, e.g. 19% at 100°C. After switching off the peroxide stream and leaving the specimen overnight in air, the decomposition on starting the following morning had fallen again, to 8%.

During a run in $H_2O_2$ vapour of 90 minutes duration, the activity fell steadily from 8% to 6.5%. The slip was then removed and heated at 500°C in air, for two hours. On testing at 100°C, a decomposition of about 2% was initially recorded, falling to zero in ten minutes. The slip was again removed, treated in hydrogen as above, and quickly returned to the flow apparatus. Immediate decomposition of 23% was found at 100°C. This remained practically constant for two hours at which time 21% decomposition was recorded.

Tin, unlike activated aluminium, became very rapidly poisoned during the course of continuous exposure to $H_2O_2$ vapour. For example, original decompositions of 40-55% registered at 140°C, fell to zero in the course of 80-85 minutes. With this behaviour it was difficult to establish the reaction order on tin/tin oxide, since on making a concentration change almost immediate poisoning of the catalyst occurred.

The order with aluminium/aluminium oxide was determined on freshly activated surfaces and the results are given in Table 10.

TABLE 10. Determination of reaction order on freshly activated $Al/Al_2O_3$ surfaces.

| Temperature of run (°C) | $H_2O_2$ concentration (mm. Hg.) | Percentage Decomposition | Time from start of run (mins.) | Remarks |
|---|---|---|---|---|
| 138 | 0.96 | 20.8 | 5 | |
| 138 | 0.96 | 20.7 | 15 | First order kinetics |
| " | 0.32 | 20.7 | 20 | |
| " | 0.32 | 21.7 | 25 | |
| " | 0.32 | 20.9 | 30 | |
| " | 0.32 | 20.7 | 35 | |
| " | 0.32 | 20.7 | 40 | Steady decomposition |
| " | 0.64 | 8.9 | 45 | Deactivation |
| " | 0.64 | 8.7 | 55 | Steady decomposition |
| " | 0.32 | 8.9 | 60 | |
| " | 0.32 | 20.7 | 65 | Catalyst Recovery |
| " | 0.32 | 20.7 | 75 | |
| " | 0.64 | 7.9 | 80 | Deactivation |
| " | 0.64 | 8.4 | 90 | Steady decomposition |
| " | 0.96 | 6.8 | 95 | Deactivation |
| " | 0.96 | 0.0 | 100 | Poisoned |
| " | 0.96 | 0.0 | 120 | " |

TABLE 10 (Continued)

| Temperature of run (°C) | $H_2O_2$ concentration (mm Hg.) | Percentage Decomposition | Time from start of run (mins) | Remarks |
|---|---|---|---|---|
| 138 | 0.96 | 23.2 | 5 | |
| " | 0.96 | 21.8 | 15 | ) First ) order |
| " | 0.64 | 22.7 | 20 | ) Kinetics |
| " | 0.64 | 21.9 | 25 | |
| " | 0.64 | 21.8 | 35 | ) First ) order |
| " | 0.32 | 22.1 | 40 | ) kinetics |
| " | 0.32 | 21.8 | 55 | |
| " | 0.64 | 9.7 | 60 | Deactivation |
| " | 0.64 | 8.3 | 65 | " |
| " | 0.96 | 7.4 | 70 | " |
| " | 0.96 | 2.8 | 75 | " |
| " | 0.96 | 0.0 | 80 | Poisoned |
| " | 0.96 | 0.0 | 95 | " |
| 181 | 0.88 | 89.6 | 5 | |
| " | 0.88 | 89.1 | 10 | ) First ) order |
| " | 0.59 | 87.6 | 15 | ) kinetics |
| " | 0.59 | 90.1 | 20 | |
| " | 0.59 | 88.8 | 25 | |
| " | 0.59 | 87.9 | 30 | Steady decomposition. |

TABLE 10 (Continued)

| Temperature of run (°C) | $H_2O_2$ concentration (mm Hg.) | Percentage Decomposition | Time for start of run (mins.) | Remarks |
|---|---|---|---|---|
| 181 | 0.59 | 87.9 | 40 | )First |
| " | 0.29 | 88.6 | 45 | )order )kinetics |
| " | 0.29 | 88.1 | 50 | |
| " | 0.29 | 88.1 | 55 | Steady decomposition |
| " | 0.59 | 71.5 | 60 | Deactivation |
| " | 0.59 | 59.4 | 65 | " |
| " | 0.59 | 47.6 | 70 | " |
| " | 0.59 | 47.5 | 75 | Steady decomposition |
| " | 0.88 | 42.3 | 80 | Deactivation |
| " | 0.88 | 39.3 | 85 | " |
| " | 0.88 | 39.3 | 95 | Steady decomposition |
| 183 | 0.29 | 90.1 | 15 | |
| " | 0.59 | 66.6 | 20 | Fast deactivation |
| " | 0.59 | 63.4 | 25 | Deactivation |
| " | 0.59 | 63.4 | 35 | Steady decomposition |
| " | 0.88 | 52.1 | 40 | Deactivation |
| " | 0.88 | 50.9 | 45 | " |
| " | 0.88 | 50.9 | 55 | )Steady )decomposition |
| " | 0.59 | 51.7 | 60 | )First order )kinetics |
| " | 0.59 | 51.2 | 65 | |
| " | 0.59 | 51.1 | 75 | )Steady decom- )position |
| " | 0.29 | 51.3 | 80 | )First order kinetics. |

TABLE 10 (Continued)

| Temperature | $H_2O_2$ concentration | Percentage Decomposition | Time for start of run (mins.) | Remarks |
|---|---|---|---|---|
| 183 | 0.29 | 51.2 | 95 | Steady Decomposition. |

The variations in the kinetic behaviour of the aluminium surfaces is somewhat analogous to that found with iron/iron oxide, in that in runs of decreasing $H_2O_2$ concentration first order kinetics were observed without the intervention of initial efficiency increases indicative of an apparent zero order process. In addition, $Al/Al_2O_3$ (activated) showed a marked deactivation, and even poisoning at the lower temperatures, on making fast increases of $H_2O_2$ concentration.

Temperature coefficient.

The experimental values found for the activation energy of the reaction on $Sn/SnO_2$ and $Al/Al_2O_3$ (activated) was found by assuming first order kinetics and making quick temperature changes as shown:-

TABLE 11. Experimental activation energies - Class (3) metal/metal oxides.

Partial pressure $H_2O_2$ = 0.88 mm. Hg.

| Metal/Metal Oxide | Temperature change (°C) | | Decomposition Change (%) | | Activation Energy (K.cals/mol.) |
|---|---|---|---|---|---|
| $Al/Al_2O_3$ (normal) | 183 | 100 | <2.0 | 0 | - |
| $Al/Al_2O_3$ (activated) | 100 | 136 | 6.0 | 43 | 18.4 |
| " | 136 | 183 | 37.0 | 98.5 | 18.3 |
| " | 100 | 136 | 7.0 | 42.0 | 18.1 |
| " | 136 | 183 | 24.0 | 92.0 | 18.7 |
| " | 183 | 136 | 90.0 | 20.0 | 19.1 |

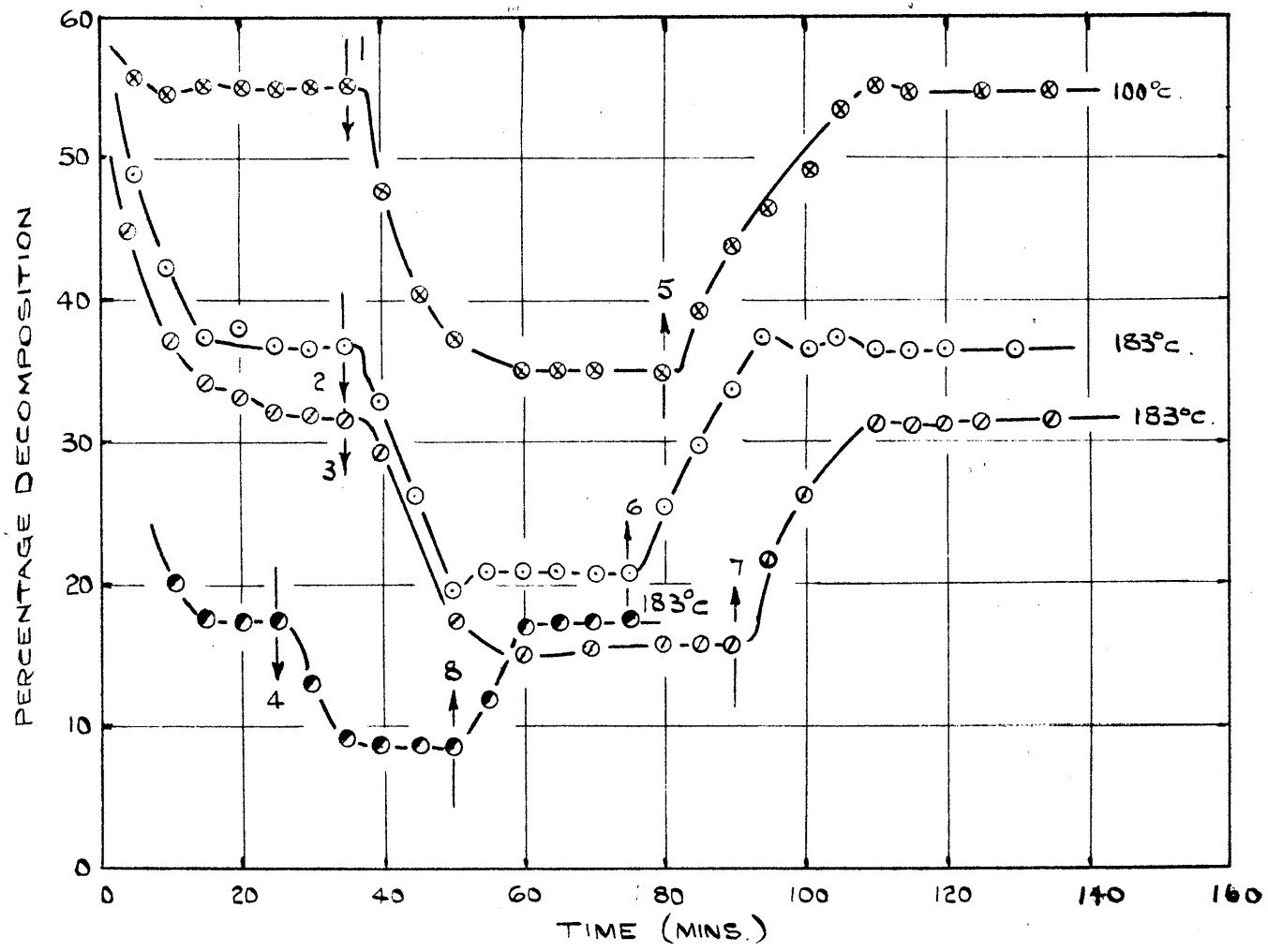
| Metal/Metal Oxide | Temperature change (°C) | | Decomposition change (%) | | Activation Energy (K.cals/mol) |
|---|---|---|---|---|---|
| $Sn/SnO_2$ | 138 | 100 | 55.0 | 3.0 | 26.8 |
| " | 100 | 138 | 4.5 | 56.0 | 26.3 |

The first three figures in Table 11 refer to the same specimen before and after hydrogen treatment. The next three were obtained with a separately prepared, hydrogen treated slip.

(c) The influence of oxygen and water vapour on metal slip catalysis.

The effect of added water vapour and oxygen on the reaction rate was examined with Fe, Co, Al (activated) and Ni slips. In all the experiments the effect of adding $H_2O$ vapour was to decrease the decomposition. This deteriorating action increased with increasing partial pressure of water in the gas phase.

Fig. 24(a) shows the general pattern of the rate changes induced by adding water vapour with the various catalysts, and Table 12 gives the steady experimental decomposition values at the various water vapour partial pressures. As Fig. 24(a) shows, short periods of 10-20 minutes were necessary for equilibrium to be attained. No permanent effect of water addition was discovered.




EFFECT OF WATER VAPOUR ON REACTION RATE.

p.p. $H_2O_2$ = 0·48 M.M. Hg.

p.p. $H_2O$ = 5·05 " Hg (ADDED).

$H_2O$ ADDED AT POINTS 1, 2, 3, 4.

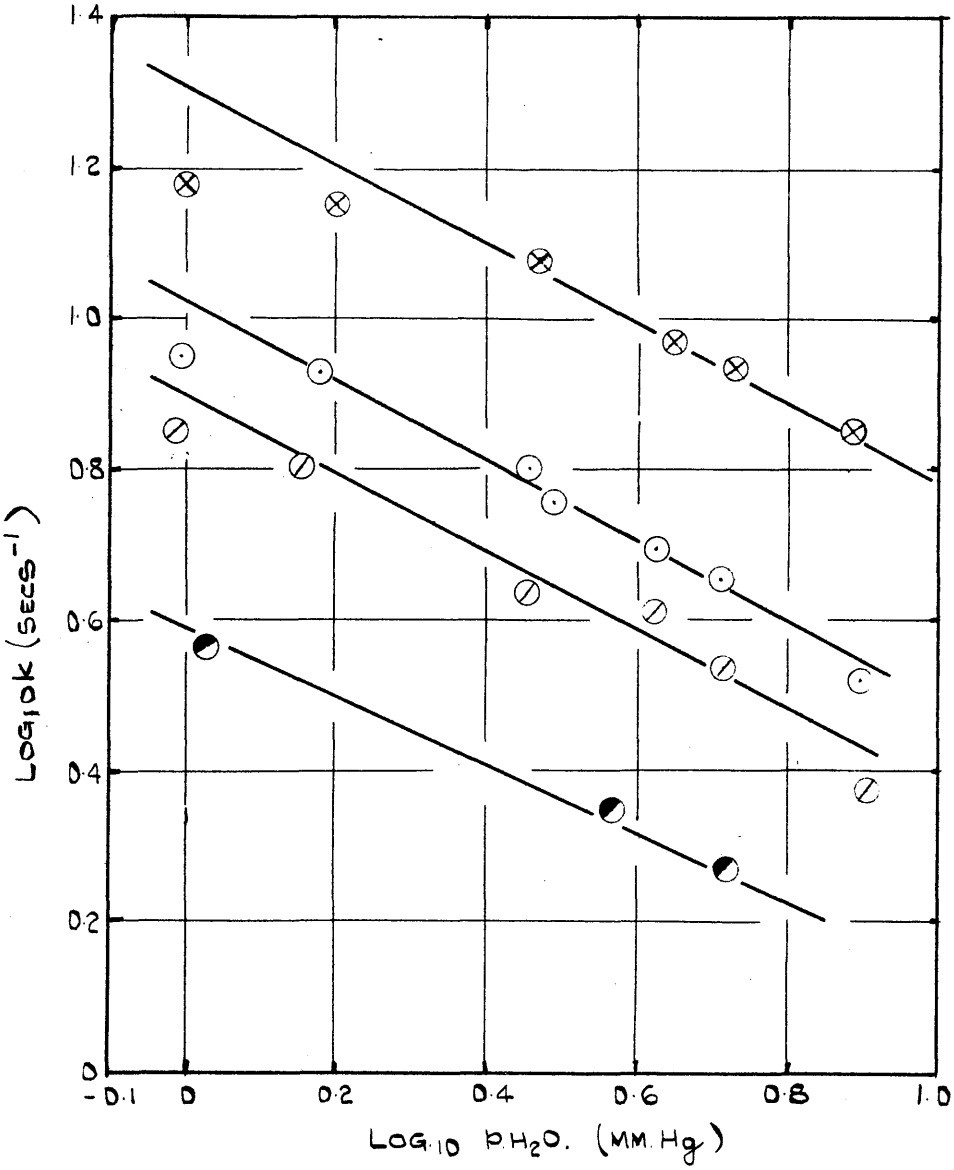
$H_2O$ REMOVED AT POINTS 5, 6, 7 8.

⊗ = Co/CoO; ⊙ Ni/NiO ; ∅ Fe/FeO/$Fe_2O_3$ ◐ Al/$Al_2O_3$ (ACTIVATED)

FIG. 24(a)

TABLE 12. Influence of varying amounts of water vapour on the reaction rate. Partial pressure $H_2O_2$ = 0.48 mm. Hg.

| Catalyst | Temperature of Run (°C) | Steady Decomposition (%). No $H_2O$. | Partial pressure $H_2O$ added (mm Hg.) | Steady Decomposition (%) with $H_2O$ |
|---|---|---|---|---|
| Ni/NiO | 183 | 38.1 | 7.58 | 14.9 |
| " | " | 36.8 | 5.05 | 20.9 |
| " | " | 37.6 | 4.06 | 22.5 |
| " | " | 36.9 | 2.85 | 25.2 |
| " | " | 37.1 | 2.72 | 27.6 |
| " | " | 37.6 | 1.35 | 34.0 |
| " | " | 37.1 | 0.78 | 35.7 |
| Co/CoO | 100 | 54.2 | 7.58 | 30.3 |
| " | " | 54.5 | 5.05 | 35.4 |
| " | " | 54.8 | 4.06 | 38.1 |
| " | " | 54.5 | 2.71 | 45.4 |
| " | " | 54.8 | 1.35 | 49.4 |
| " | " | 54.5 | 0.78 | 53.3 |
| Fe/FeO/$Fe_2O_3$ | 183 | 31.7 | 7.58 | 10.7 |
| " | " | 31.8 | 5.05 | 16.0 |
| " | " | 32.7 | 4.06 | 19.0 |
| " | " | 32.9 | 2.71 | 23.1 |
| " | " | 32.9 | 1.35 | 27.4 |
| " | " | 32.3 | 0.78 | 28.9 |




VARIATION OF RATE CONSTANT WITH WATER VAPOUR PRESSURE

⊗ OXIDISED COBALT SLIPS (100°c)
⊙ OXIDISED NICKEL SLIPS (183°c)
⊘ OXIDISED IRON SLIPS (183°c)
◐ FRESHLY ACTIVATED ALUMINIUM SLIPS (183°c)

FIG. 24 (b)

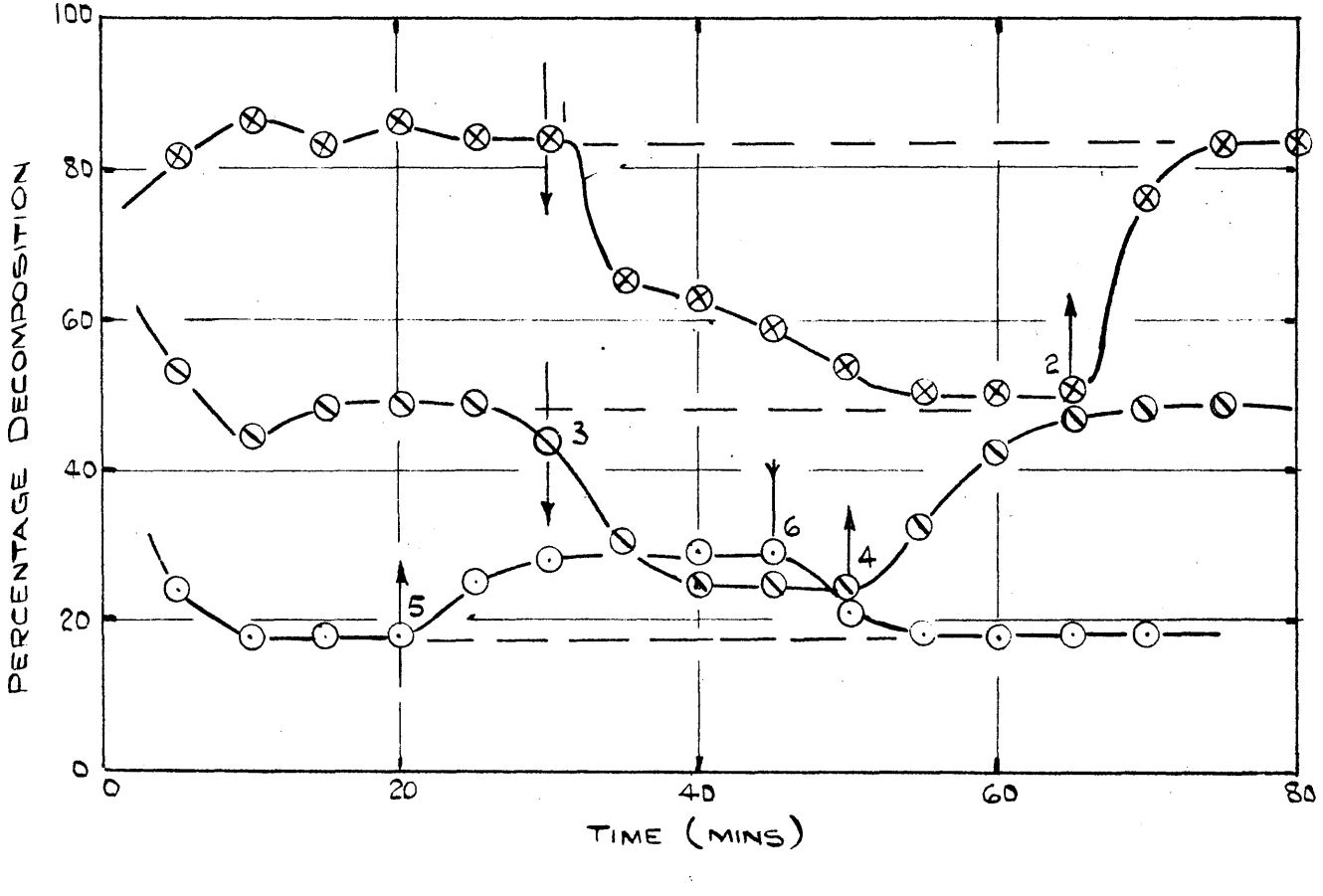
TABLE 12 (Continued)

| Catalyst | Temperature of Run (°C) | Steady Decomposition (%). No $H_2O$. | Partial pressure $H_2O$ added (mm Hg) | Steady decomposition (%) with $H_2O$ |
|---|---|---|---|---|
| $Al/Al_2O_3$ (activated) | 183 | 17.4 | 5.05 | 8.5 |
| " | " | 17.4 | 3.80 | 10.8 |
| " | " | 17.4 | 0.78 | 16.7 |

In Fig. 24(b) $\log_{10}$ (rate constant) of the steady decompositions in Table 21 are plotted against $\log_{10}$ (p.p.$H_2O$), where the partial pressures of water vapour are those of the total pressure of water vapour present in the system; found by adding the partial pressure of the water vapour arising from the decomposition to the values in column 4 of the above table. A series of straight, parallel lines could be drawn of gradient -0.5 with some deviation, especially for the more active surfaces at the lower p.$H_2O$. This suggests that the decomposition rate varies approximately inversely with the square root of the water vapour pressure,

$$\text{i.e. Rate} \left( - \frac{d\left[H_2O_2\right]}{dt} \right) \propto (pH_2O)^{-0.5}$$

The experimental set-up did not allow for the evaluation of the rate constant with varying quantities of oxygen in the gas stream. The nitrogen carrier was replaced totally by pure oxygen. Then, by determining the rate with oxygen and that with nitrogen (plus oxygen produced in the decomposition), an indication of the role of oxygen was obtained. In all cases the decomposition was accelerated by oxygen. This procedure was carried out for each specimen at two different temperatures. The pattern of the acceleration is shown in Fig. 25(a)., whilst the steady decomposition




INFLUENCE OF OXYGEN ON REACTION RATE.

⊗ OXIDISED NICKEL SLIP (183°C).
⊘ " " " (139°C).
⊙ FRESHLY ACTIVATED ALUMINIUM SLIP (140°C).

POINTS 1,3 & 6. OXYGEN CARRIER → NITROGEN CARRIER.
" 2,4 & 5 NITROGEN " → OXYGEN " .

FIG. 25(a)

values are given in Table 13.

TABLE 13. Influence of added oxygen on the reaction rate.

(p.p. $H_2O_2$ = 0.96 mm. Hg).

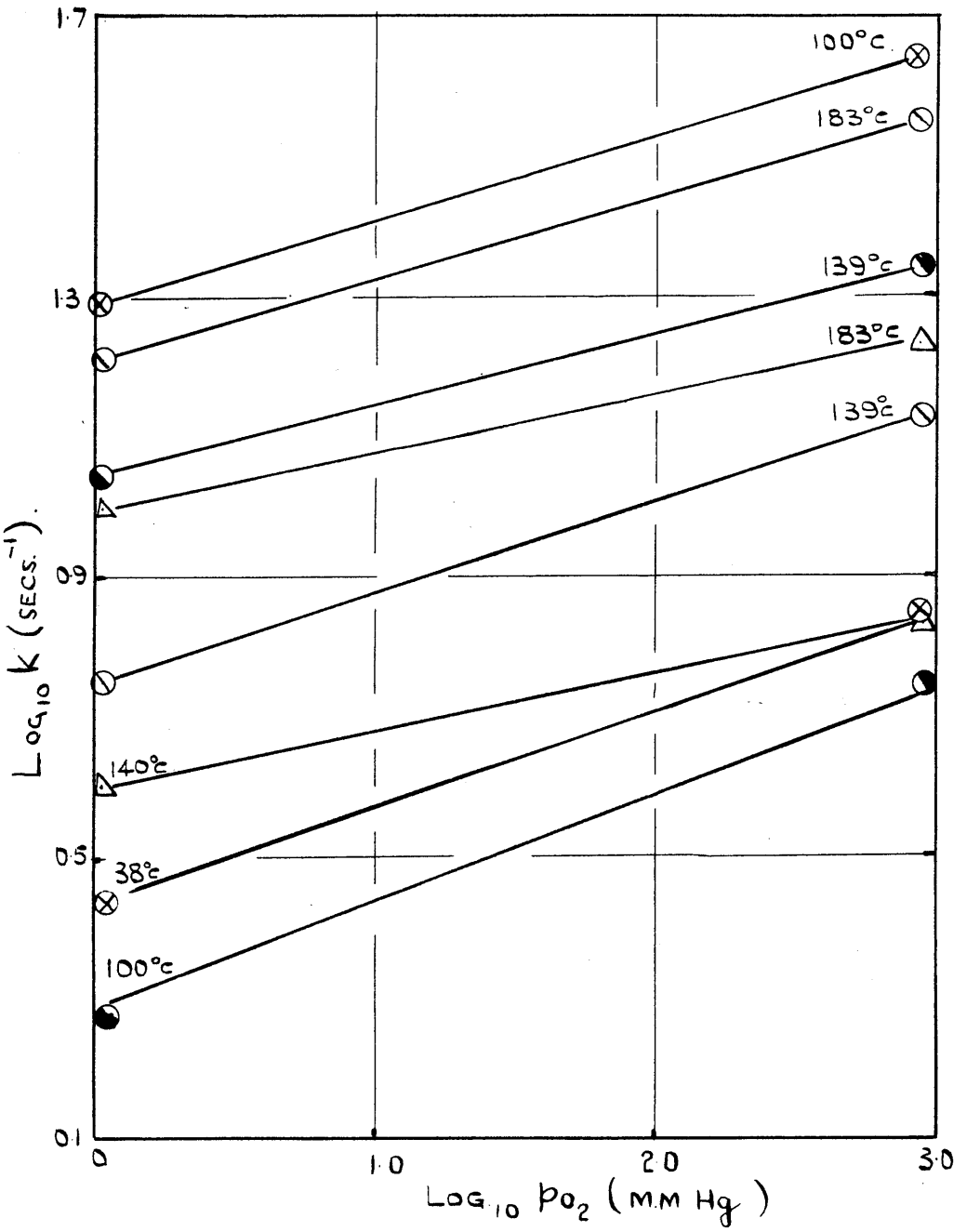
| Catalyst | Temperature of Run (°C) | Steady % decomposition ($O_2$ carrier) | Steady decomposition ($N_2$ carrier) |
|---|---|---|---|
| Ni/NiO | 183 | 83.1 | 55.6 |
| " | 139 | 48.2 | 24.0 |
| Al/$Al_2O_3$ (act) | 183 | 58.1 | 41.5 |
| " | 140 | 28.9 | 18.0 |
| Co/CoO | 78 | 88.9 | 63.1 |
| " | 38 | 39.2 | 13.2 |
| Fe/FeO/$Fe_2O_3$ | 139 | 66.6 | 41.5 |
| " | 100 | 25.6 | 6.9 |

Fig. 25(a) shows that replacing oxygen by nitrogen as the carrier caused the catalyst efficiency to deteriorate to its original level. (Removing the added water vapour allowed the catalyst to recover - Fig. 24(a) ).

In Fig. 25(b), $\log_{10} k$ is plotted against $\log_{10} (p.p.O_2)$. The slope of the lines for the activated Al/$Al_2O_3$ catalysts is 0.08. The reaction rate on the other catalysts was accelerated by oxygen addition to a slightly greater extent and the slopes of these lines, which are nearly all parallel, lie between 0.12 and 0.13 and may be taken as 1/8.

$$\text{Hence, Rate} \propto (pO_2)^{1/8}$$

for the class (1) and class (2) metal/metal oxides.




EFFECT ON CATALYSIS OF REPLACEMENT OF $N_2$ BY $O_2$ AS THE CARRIER GAS

- ⊗ Co/CoO;
- ⊘ Ni/NiO
- ◔ Fe/FeO/$Fe_2O_3$
- △ "ACTIVATED" Al/$Al_2O_3$

FIG. 25(b)

For the metal/metal oxides of classes (1) and (2), the dependance of the catalysis rate on $H_2O_2$, $H_2O$ and $O_2$ may then be represented in the form of the following equation:-

$$-\frac{d[H_2O_2]}{dt} = K \cdot \frac{[H_2O_2] \cdot pO_2^{1/8}}{pH_2O^{\frac{1}{2}}}$$

(3) Catalysis on pure oxide slips.

The catalysis was studied on a range of bulk oxides prepared as already described under materials.

These included a wide range of single oxides, mixed oxides of the type $XO/Y_2O_3$ and oxides containing trace impurities. It is proposed to deal with these separately, commencing with pure single oxides which, like the metal/metal oxide specimens, may be subdivided into three activity classes: viz:-

I. NiO; PbO; $Mn_2O_3$; $Co_3O_4$ - Very active catalysts.

2. ZnO; CdO; CuO; $Fe_2O_3$ - Fairly active catalysts.

3. MgO; $\alpha$ - $Al_2O_3$ - Inactive catalysts.

Class I.

This group comprises those oxides found to be most active.

Nickel Oxide.

Special attention was given to this oxide because of the interesting differences between the green and black preparations. If the oxide is prepared below 400°C it has a black appearance and contains an excess of oxygen, which may be as much as 16% by weight estimated on the bulk. (This may, of course, be differentially distributed as between the bulk and the surface of a given particle.) If the preparation is carried out above 600°C and quickly cooled to room temperature, an apple-green oxide results which on analysis showed no deviation from stoichiometry. This is illustrated in the following results obtained by analysis with dimethylglyoxime:-

TABLE 14. Analytical results for "green" and "black" nickel oxide.

| Wt.of Nickel Oxide (gm.) | Wt.of Nickel in complex (gm.) | Wt.of oxygen in oxide (gm.) | Mols.Nickel in oxide | $\frac{1}{2}$ Mols oxygen in oxide | Ratio Nickel to oxygen |
|---|---|---|---|---|---|
| 0.05940 | 0.04504 | 0.01436 | $77 \times 10^{-5}$ | $89.9 \times 10^{-5}$ | 1:1.165 |
| 0.10720 | 0.08126 | 0.02594 | $139 \times 10^{-5}$ | $162 \times 10^{-5}$ | 1:1.168 |
| 0.30510 | 0.24000 | 0.06510 | $40.8 \times 10^{-4}$ | $40.8 \times 10^{-4}$ | 1:1.000 |

The first two results refer to "black" NiO and the third to "green" NiO. This detail was expanded further by magnetic susceptibility and X-ray measurements and the results are given below.

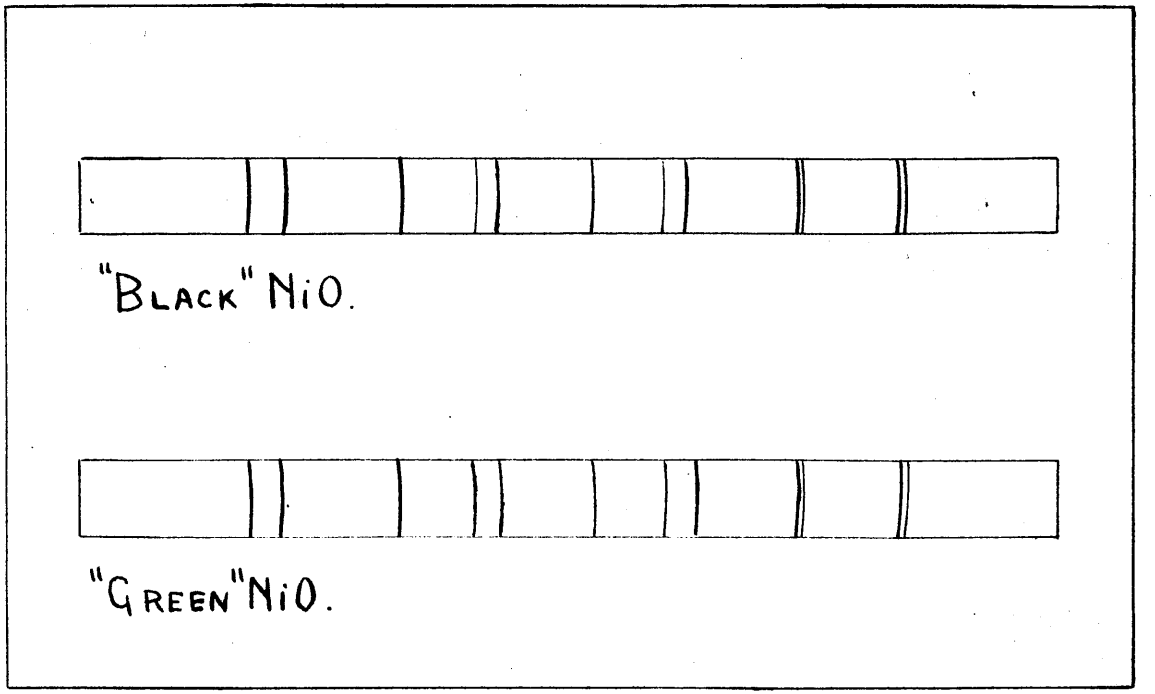
(a) Structural investigation of "green" and "black" NiO.

The magnetic susceptibility results are shown in Table 15.

TABLE 15 Magnetic susceptibilities of "black" and "green" NiO at 20°C.

| Oxide | Magnetic Susceptibility (c.g.s. units) | | Extrapolated Value (infinite field) | Field Strength Dependance |
|---|---|---|---|---|
| | 10,600 oersteds | 1,500 oersteds | | |
| NiO(green) | $9.63 \times 10^{-6}$ | $10.05 \times 10^{-6}$ | $9.63 \times 10^{-6}$ cgs. units. | Independant |
| NiO(green) | $9.63 \times 10^{-6}$ | $10.09 \times 10^{-6}$ | $9.63 \times 10^{-6}$ cgs. units. | Independant |
| NiO(black) | $12.25 \times 10^{-6}$ | $18.78 \times 10^{-6}$ | $11.00 \times 10^{-6}$ cgs. units. | Ferro-magnetic. |
| NiO(black) | $12.70 \times 10^{-6}$ | $18.01 \times 10^{-6}$ | $11.20 \times 10^{-6}$ cgs. units. | Ferro-magnetic. |

The determinations were made on four different samples and the values given above are the average of three determinations at each




X-Ray Powder Photograph Patterns.
"Green" And "Black" Nickel Oxides.

FIG.B

field strength for every sample. The value found at 1,500 Oersteds for the "green" NiO was so slightly different from the value at 10,600 Oersteds, that this latter value has been taken as correct. In any case if this was a real difference between the two determinations then the ferromagnetism was very slight in comparison to that of "black" NiO.

This ferromagnetic behaviour of "black" NiO seemed to indicate the presence of metallic nickel in the oxide as has been postulated by Klemm and Hass (107) and supported by Selwood (108); but on making three separate X-ray examinations, with $CuK_{\alpha}$ radiation in a powder camera, of separately packed "black" NiO specimens no trace of metallic nickel was detected. The X-ray powder photograph patterns are shown in Fig. B. opposite.

In these experiments a 9 cm. camera was used with a 0.25 mm. diameter specimen packed in a Lindemann glass phial. The position of the various arcs on the photograph was measured by a travelling microscope to 0.001 mm. and from this data the d values were found from the Bragg equation:-

$$d/n = \lambda/2 \sin\theta .$$

By the usual method using a master graph of a cubic crystal, a=0 - 8A°, the d values of the two oxides were found to correspond to crystals of unit cell size, 4.15 - 4.2A°.

At the widest angle of reflection registered on the powder photographs, for "green" i.e. stoichiometric NiO, $d_{10} = d_{333} = 0.805$.

$\therefore$ Unit cell size $= 0.805 \ (h^2+k^2+l^2)^{\frac{1}{2}}$

$= \underline{\underline{4.183A^{\circ}}}$

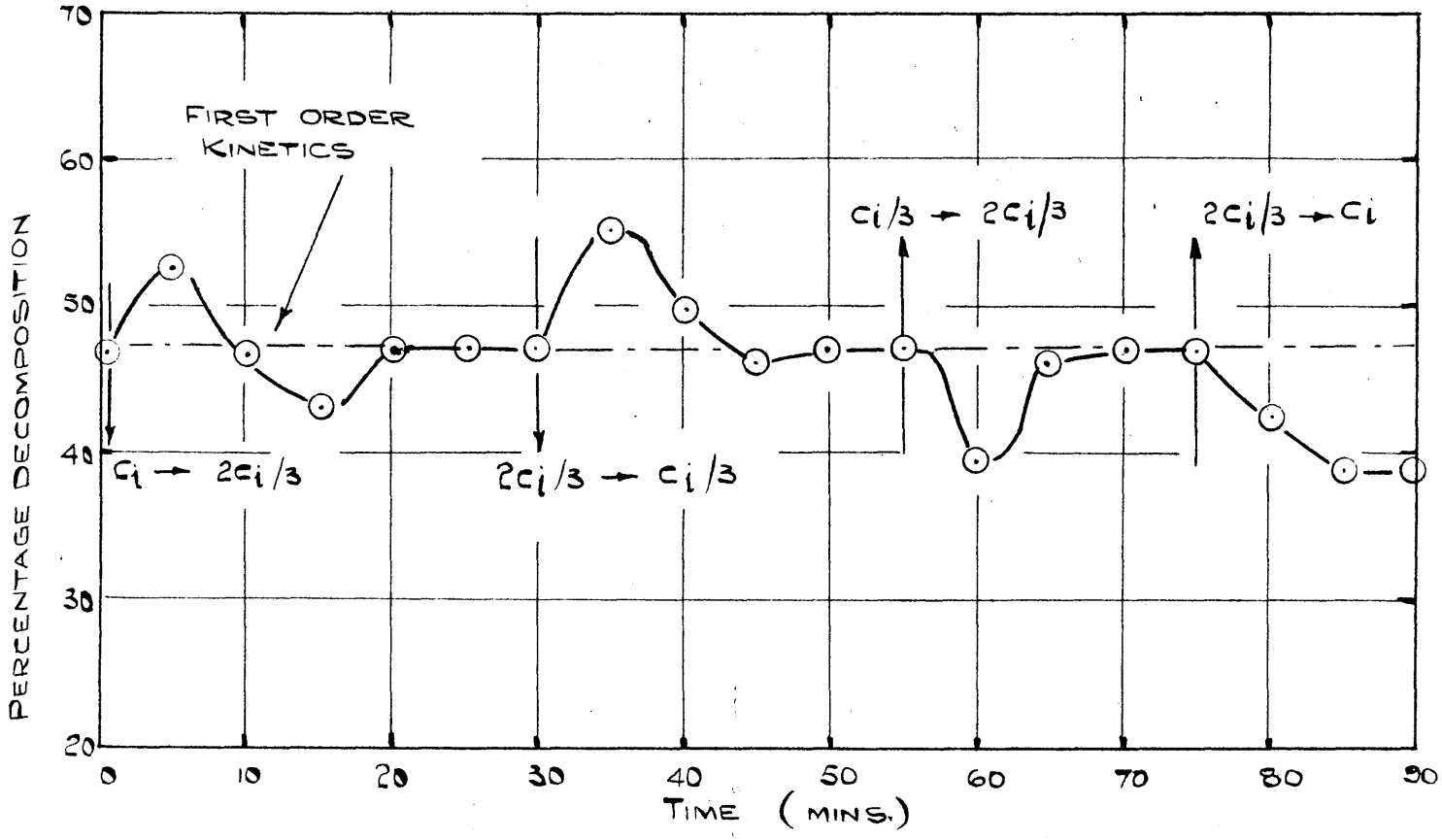
and for "black" NiO, $d_{10} = d_{333} = 0.801$.

$\therefore$ Unit cell size $= \underline{\underline{4.162A^{\circ}}}$.

The value for "green" NiO is similar to that found by Fensham (119), a = 4.181A°, and is slightly larger than that given in the A.S.T.M. index for "nickel monoxide" i.e. 4.172A°.

The literature on the structural and magnetic properties of nickel oxide contains many anomalies, arising from the fact that the excess of oxygen accommodated in the oxide is a variable factor dependant on the method and temperature of preparation. In many cases (99) no allowance has been made for the possibility of hydrate formation in the subsequent analysis or in heat treatment, which has led to the postulation of formulae such as $Ni_2O_3$ and $NiO_2$ (109). The existence of such structures however, remains doubtful (110). That NiO can be prepared in a stoichiometric ratio of nickel to oxygen is evident from this work and that of Bhatnagar and Bal (111).

That "black" nickel oxide is ferromagnetic in character is established; but on the basis of magnetic evidence alone it is hardly justifiable to assume that this is due to the presence of metallic nickel. The ferromagnetism may rather be due to the high oxygen content, which has recently also been postulated by Perakis et al. (112), and the slightly smaller unit cell size, reported here for "black" NiO (i.e. $NiO_{1.165}$) can be accounted for on the basis of the oxygen excess being



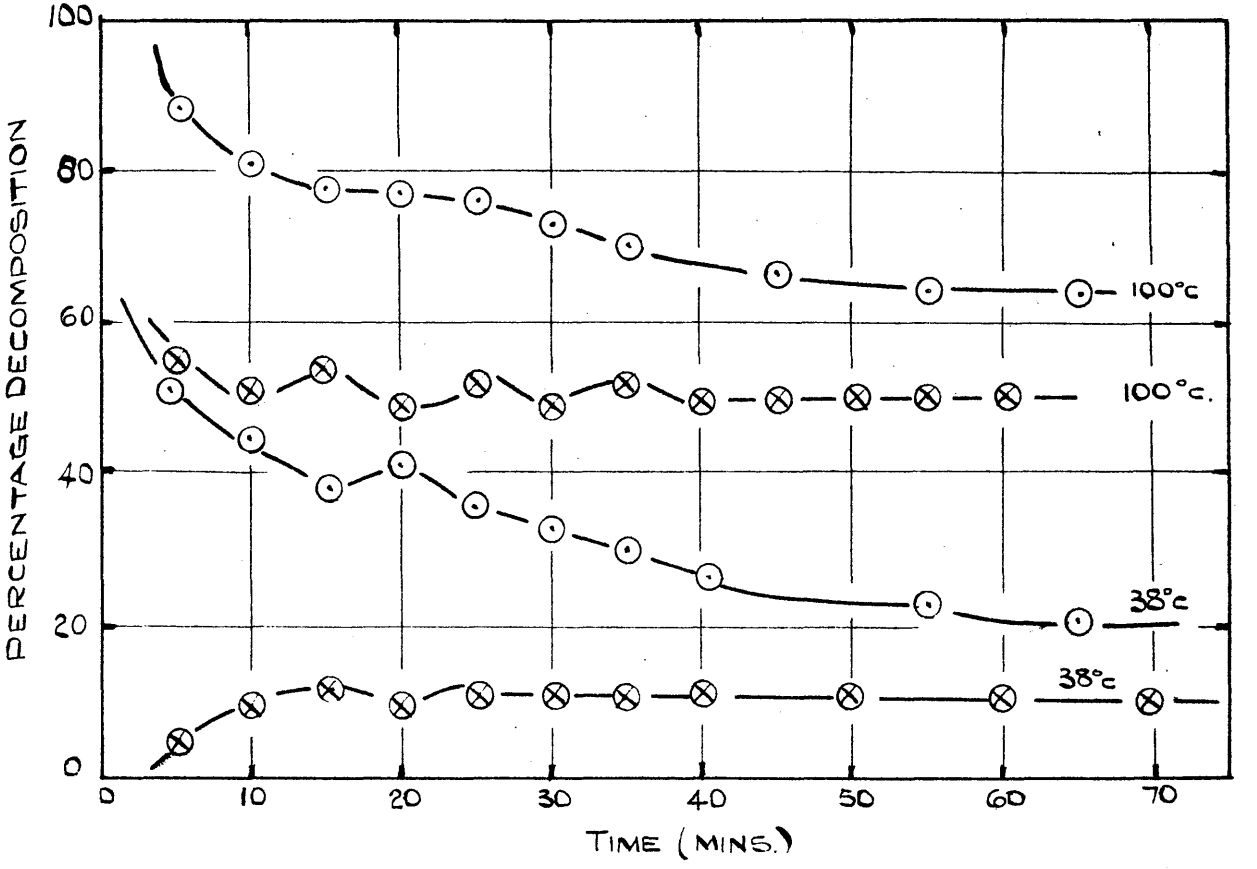

RAPID CONCENTRATION CHANGES "GREEN" NICKEL OXIDE AT 100°C. ($c_i$ = 0·88 mm Hg)

FIG. 26

accommodated by a balanced proportion of vacant cation sites throughout the lattice, affording the possibility of lattice distention.

(b) Catalysis on nickel oxide slips.

Both the "black" and "green" nickel oxides were quite active towards $H_2O_2$ vapour. The "black" oxide on first exposure to the substrate gave a high decomposition rate but over the course of a run at 100°C of 90 minutes duration the "black" NiO changed colour to a murky green, and tended towards the efficiency level of the stoichiometric oxide. Because of the rapidity of this continuous deactivation, it was not possible to determine the reaction order on "black" NiO with any satisfaction. Fig. 26 illustrates the behaviour, similar with both oxides at the steady efficiency value, on making fast concentration changes, to determine the reaction order at 100°C. The change from Ci(0.88 mm Hg. p.p. $H_2O_2$) to 2/3 Ci was accompanied by an efficiency cycle before the rate settled to the same steady value as initially exhibited at Ci, but the earliest indication after a change was of a first order process, and remained so after a similar fluctuation in the change to Ci/3. The reverse change to 2 Ci/3 gave the first order requirement, but on restoring the $H_2O_2$ concentration to the original Ci a smooth fall of activity was recorded which settled to a new, lower decomposition value. The efficiency cycles found with these slips had smaller amplitudes than those of the oxidised metal films, and at no time did the peaks approach a decomposition value which would have indicated zero order behaviour. However, like the metal/metal oxides the catalyst always appeared to deactivate on restoring the original concentration.




ACTIVITY DETERIORATION ON "BLACK" NiO,
AND CYCLIC CHANGES OF ACTIVITY ON "GREEN" NiO.

"GREEN" NiO. = ⊗

"BLACK" NiO. = ⊙

FIG. 27

Temperature coefficient of decomposition on NiO.

No two specimens of the non-stoichiometric NiO gave precisely the same temperature coefficient. This was possibly due to the continuous change on exposure to hydrogen peroxide vapour. The values found lay in the range 4-8K.cals/mol. The tendency was always to settle at the value of "green" NiO which was 7-8 K.cals/mol. The following table illustrates this for runs with a series of separately compacted specimens.

TABLE 16. Temperature coefficients for nickel oxide.

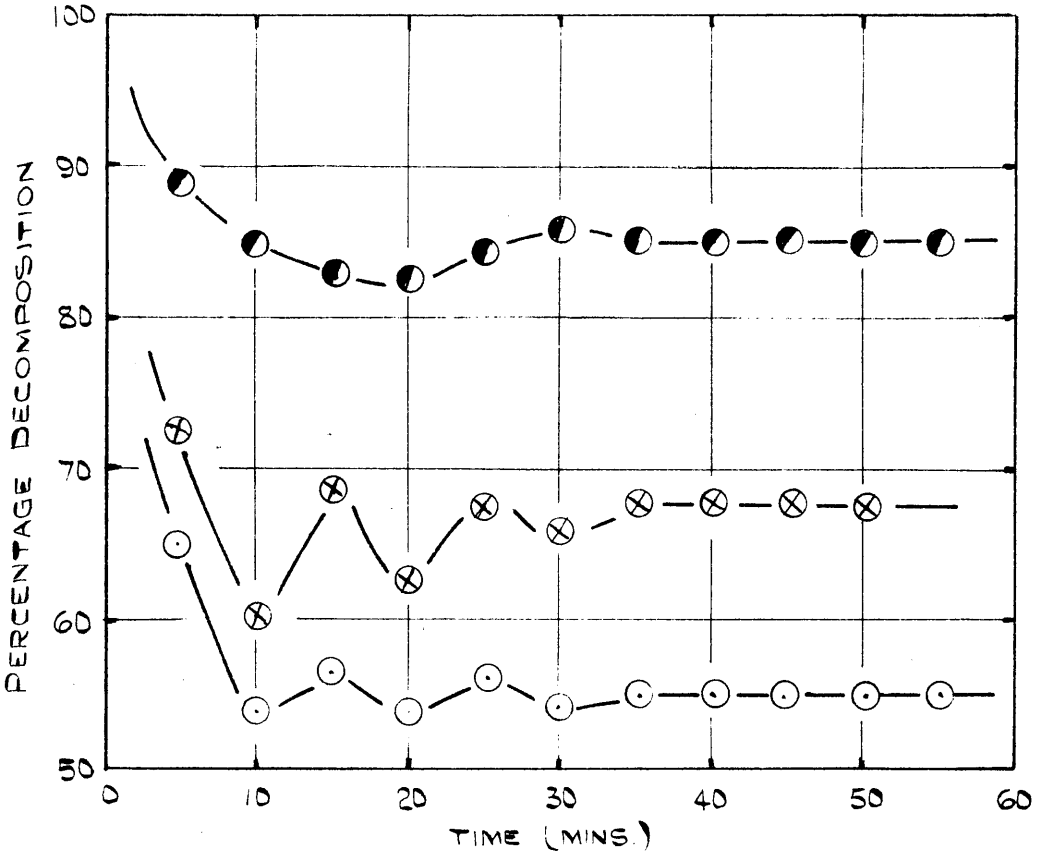
| Oxide | Temperature (°C) | | Decomposition (%) | | Temperature Coefficient (K.cals/mol.) |
|---|---|---|---|---|---|
| | $T_1$ | $T_2$ | $T_1$ | $T_2$ | |
| NiO (green) | 100 | 38 | 48 | 7 | 8.1 |
| NiO (green) | 100 | 38 | 50 | 9 | 7.5 |
| NiO (black) | 100 | 38 | 65 | 36 | 4.5 |
| NiO (black) | 100 | 38 | 70 | 46 | 4.1 |
| NiO (black/ green) | 100 | 38 | 64 | 18 | 6.8 |

The last figure refers to a specimen of "black" NiO exposed to $H_2O_2$ vapour for 40 minutes before making the temperature change.

Fig. 27 shows the initial cyclic efficiency changes given by "green" NiO, and the decay in time of the black oxide at different temperatures.

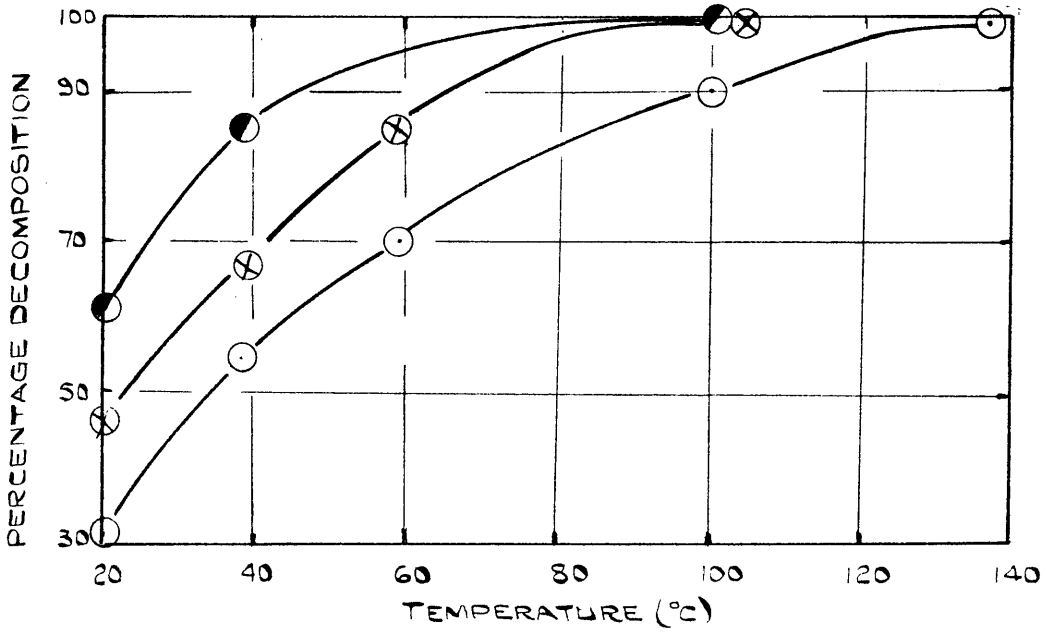
(c) PbO, $Mn_2O_3$, $CoO/Co_2O_3$.

These oxides were found to be very active catalysts in the decomposition. PbO and $Mn_2O_3$ being perhaps the most active catalysts of all the single oxides examined in this work.




SHOWING INITIAL CYCLIC CHANGES ON BULK OXIDES AT 38°C.
◐ $Mn_2O_3$ ; ⊙ $CoO/Co_2O_3$ ; ⊗ PbO.

FIG. 28.




SHOWING DECOMPOSITIONS AT VARIOUS TEMPERATURES.
OXIDES AS FIG. 28.

FIG. 29.

All the oxides showed cyclic activity variations for 25-35 minutes at a given temperature before the steady decomposition value was reached. This is illustrated in Fig. 28 for the three oxides in runs at 38°C, whilst in Fig. 29 the oxides are contrasted according to the steady decomposition given by each one at various temperatures. It can be seen from Fig. 29 that even at room temperature (20°C) the oxides were exceedingly active catalysts.

Table 17 below summarises the figures obtained for the experimental activation energies in a fast temperature change for these oxides heat treated at 600°C.

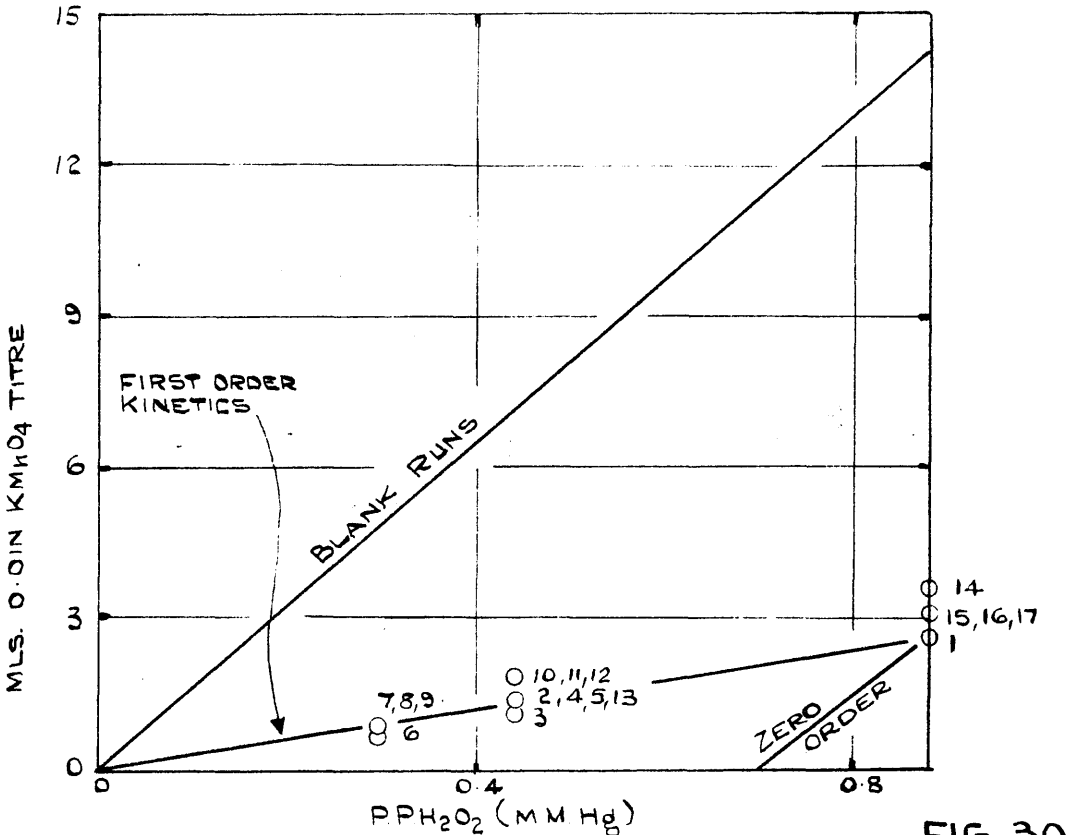
TABLE 17. Experimental activation energies, class (1) oxides. Fast temperature changes (p.p. $H_2O_2$ = 0.86 mm Hg.)

| Oxide | Temperature (°C) | | Decomposition (%) | | Experimental Activation Energy (K.cals/mol) |
|---|---|---|---|---|---|
| | $T_1$ | $T_2$ | $T_1$ | $T_2$ | |
| $Mn_2O_3$ | 59 | 37 | 95.0 | 76.5 | 6.9 |
| PbO | 58 | 38 | 84.0 | 60.0 | 6.5 |
| $CoO/Co_2O_3$ | 100 | 38 | 90.1 | 41.0 | 5.9 |

It can be seen from the above table that the activation energies for these very active catalysts do not vary much in the temperature region 100 - 38°C.

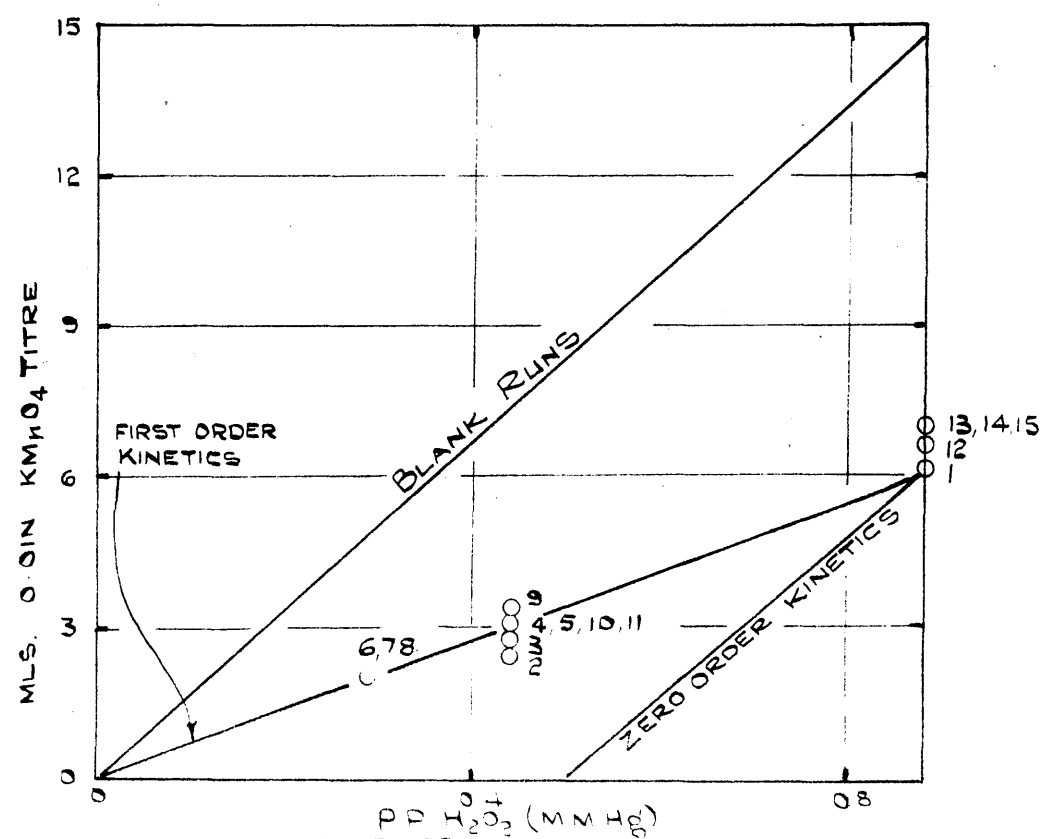
Magnetic susceptibility.

Table 18 gives the magnetic susceptibility values found for the various oxides.




DECOMPOSITION KINETICS
$Mn_2O_3$ - 37°C. POINTS AT 5 MINUTE INTERVALS

FIG. 30 (a)




DECOMPOSITION KINETICS
P.O - 38°C POINTS AT 5 MINUTE INTERVALS

FIG 30 (b)

TABLE 18. Magnetic susceptibilities at 20°C. Class (1) oxides.

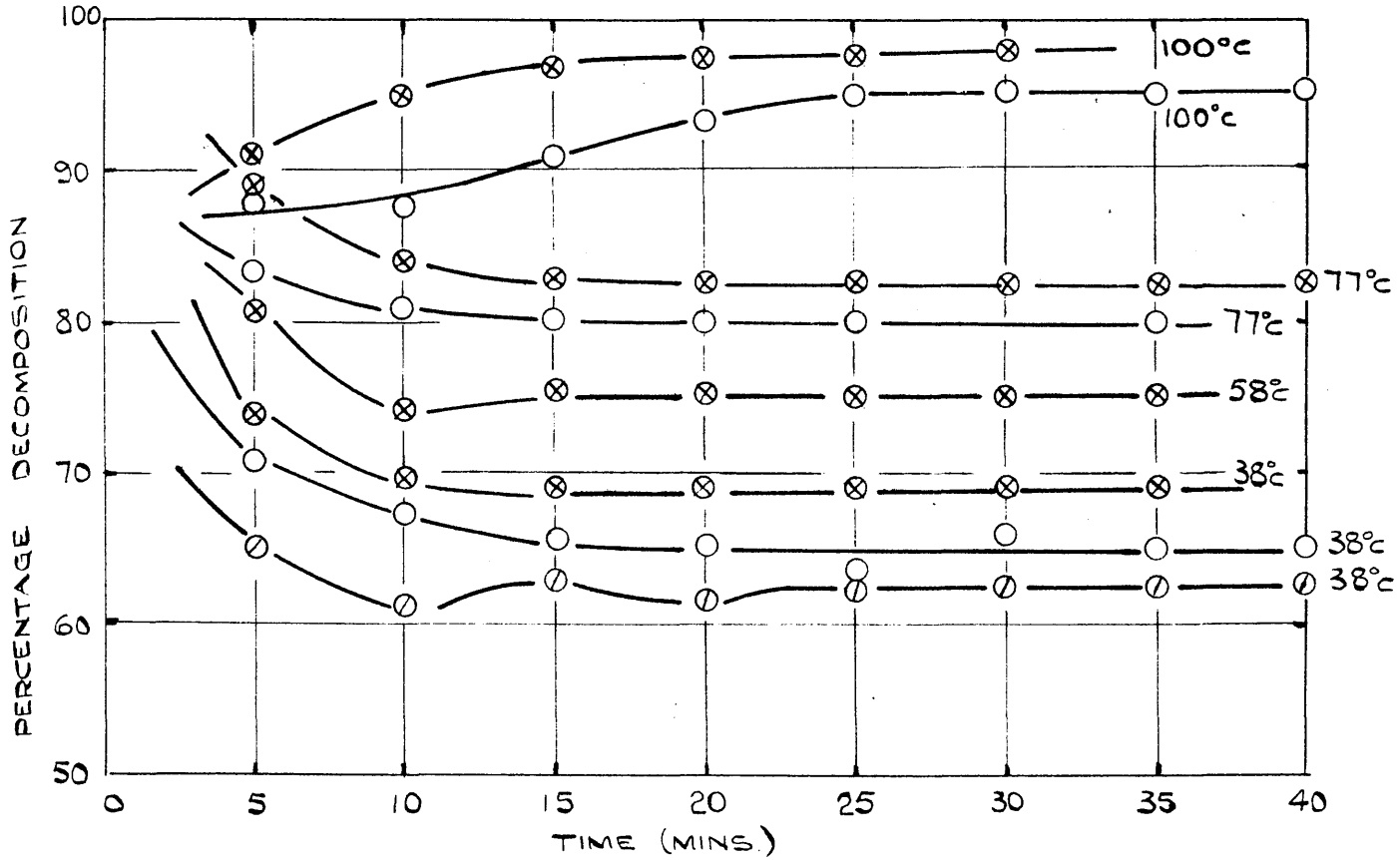
| Oxide | Magnetic Susceptibility (c.g.s. units) 10,600 oerst. | 1,500 oerst. | Extrapolated Value at infinite field. | Type |
|---|---|---|---|---|
| PbO | - | - | - | Diamagnetic |
| $Mn_2O_3$ | $92.0 \times 10^{-6}$ | $108.7 \times 10^{-6}$ | $91.0 \times 10^{-6}$ | Ferromagnetic |
| $CoO/Co_2O_3$ | $30.9 \times 10^{-6}$ | $30.9 \times 10^{-6}$ | $30.9 \times 10^{-6}$ | Paramagnetic |

Order of reaction.

The reaction kinetics were examined on $Mn_2O_3$ and PbO at 37°C. The findings are shown in Figs. 30(a) and (b) where it can be seen that the process of fast concentration changes from Ci $\longrightarrow$ Ci/3 showed no deviation from a first order relationship. The reverse changes Ci/3 $\longrightarrow$ Ci/2 $\longrightarrow$ Ci point to the same first order dependance on $H_2O_2$ concentration, a slight loss of activity being indicated at the restoration of Ci. No cyclic changes of efficiency were observed.

Influence of preparation temperature.

Manganese sesquioxide was also studied with a view to obtaining a correlation between catalytic activity and the temperature of pre-treatment in the region 300-760°C. Each sample was fired for six hours at the required temperature in an atmosphere of nitrogen. The following table summarisesthe results, with reference to the steady $H_2O_2$ decomposition value found at different temperatures for each specimen.




FIRST EXPOSURE ACTIVITY VARIATIONS ON $Mn_2O_3$
(DIFFERENT TEMPERATURES OF PRE-TREATMENT)
RUNS AT VARIOUS TEMPERATURES

○ 300°C PREPARATION ⊗ 760°C PREPARATION
⊘ 400°C PREPARATION

FIG 30.

(600°C PREPN ILLUSTRATED IN FIG. 28)

TABLE 19. $Mn_2O_3$ heat-treated at different temperatures. Steady decompositions (p.p.$H_2O_2$ = 0.86 mm. Hg).

| Temperature of Preparation (°C) | Steady Decomposition Value (%) at T°C | | | |
|---|---|---|---|---|
| | 38°C | 58°C | 77°C | 100°C |
| 300 | 65 | 70 | 80 | 95 |
| 400 | 63 | 70 | 79 | 94 |
| 600 | 85 | - | 100 | 100 |
| 760 | 69 | 75 | 82.5 | 97.5 |

N.B. The D values in the last 4 columns are not suitable for $E_A$ determinations for which rapid temperature changes are necessary.

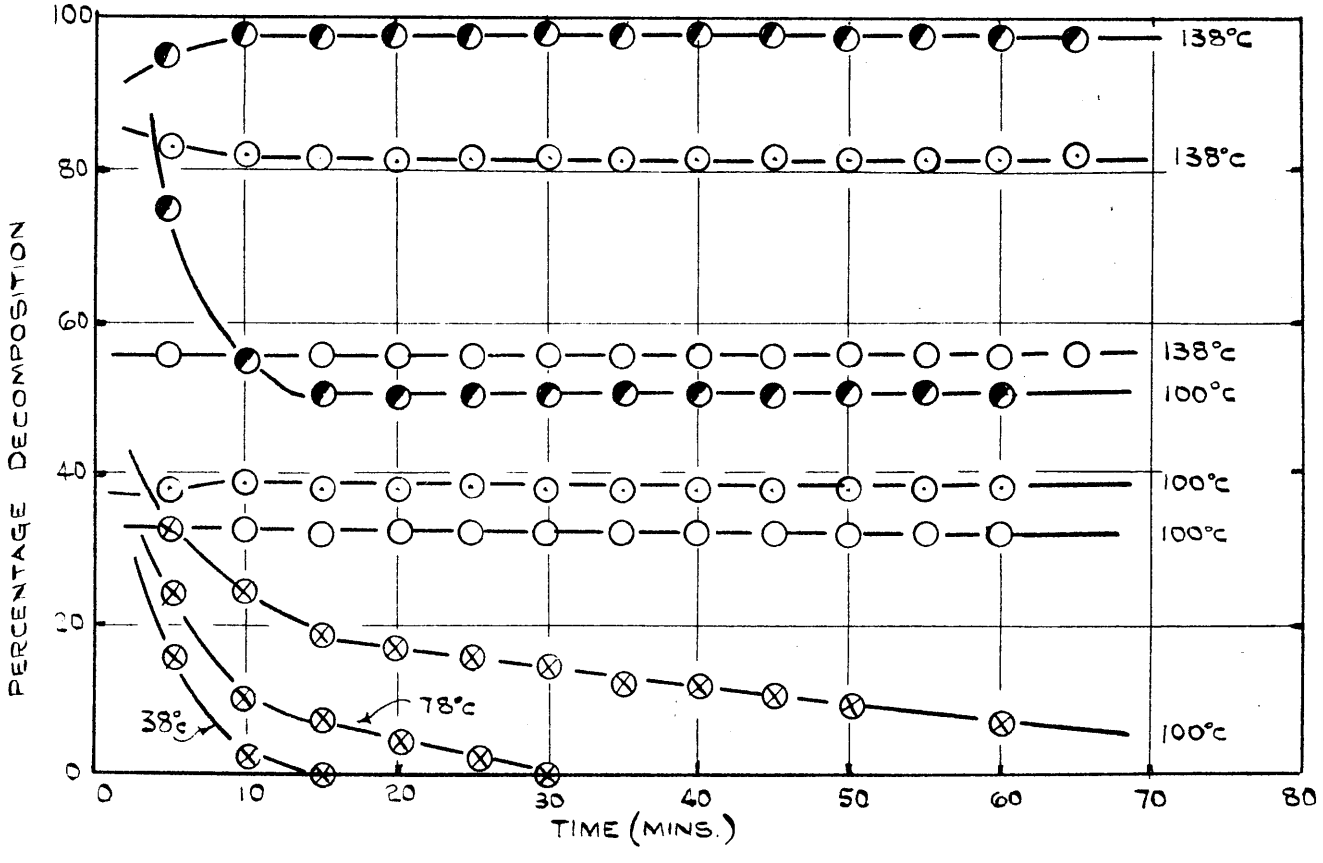
As the table shows the optimum efficiency was reached in the catalyst prepared at 600°C. There was little difference in activity between the 300 and 400°C samples, whilst the sintered 760°C sample, resembled the low temperature preparations in activity. Fig. 30 shows the initial efficiency changes of these oxides before attaining the steady value.

Magnetic susceptibility.

Table 20 sets out the magnetic susceptibility data found for the different oxides:-

TABLE 20. Magnetic susceptibility (20°C) of $Mn_2O_3$ samples.

| Temperature of Preparation (°C) | X (cgs units) x $10^{-6}$ | | | Dependance on Field Strength |
|---|---|---|---|---|
| | 10,600 oerst. | 1,500 oerst. | Infinite Field | |
| 300 | 89.0 | 88.7 | 89.0 | - |
| 400 | 89.1 | 89.1 | 89.1 | - |
| 600 | 92.0 | 108.7 | 91.0 | Slightly Ferromagnetic |
| 760 | 99.0 | >250 | 95.0 | Ferromagnetic |




DECOMPOSITION PATTERN AT VARIOUS TEMPERATURES.
CLASS (2) OXIDES.

⊗ ZnO ; ◐ CuO.
⊙ $Fe_2O_3$ ○ CdO.

FIG. 31.

There would appear from the susceptibility data to be an apparent structural change in the 600°C and 760°C samples, which is more pronounced in the latter.

(d) Class (2) ZnO; CdO; CuO and $Fe_2O_3$.

These oxides although not as active as the first class, still decomposed $H_2O_2$ (vapour) fairly readily in the temperature range 80-183°C. Table 21 summarises the experimental data obtained with this series.

TABLE 21. Steady level decompositions at various temperatures. Class (2) oxides. (p.p. $H_2O_2$ = 0.86 mm. Hg.)

| Oxide | Percentage Decomposition (STEADY LEVEL.) | | | | |
|---|---|---|---|---|---|
| | 38°C | 77°C | 100°C | 138°C | 183°C |
| CdO | 0 | 2.0 | 32.0 | 55.5 | - |
| $Fe_2O_3$ | 0 | 0 | 37.5 | 80.1 | 100 |
| CuO | 0 | 6.0 | 50.1 | 98.0 | - |
| ZnO | 0 | 0 | 14.0 | - | - |

As the table shows the oxides so not become appreciably active until 100°C, like the metal supported oxide films of Fe and Zn. Apart from ZnO, the catalysts when freshly exposed to the peroxide vapour showed no cyclic or other variation in activity; the steady value being reached almost immediately. ZnO when initially exposed to $H_2O_2$ vapour gave decompositions at 38 and 77°C which fell to zero in 10 minutes at the lower and 30 minutes at the higher temperature; similarly at 100°C the oxide slowly poisoned, as shown in Fig. 31 where this behaviour is contrasted with that of the other oxides in this group. The figures for ZnO given in the above table

were the decomposition values after 30 minutes exposure to $H_2O_2$ vapour.

Temperature coefficient.

By making fast temperature changes with these catalysts, the following figures were obtained for the temperature coefficients:-

TABLE 22. Experimental activation energies. Class (2) Oxides.

(p.p. $H_2O_2$ = 0.86 mm. Hg.)

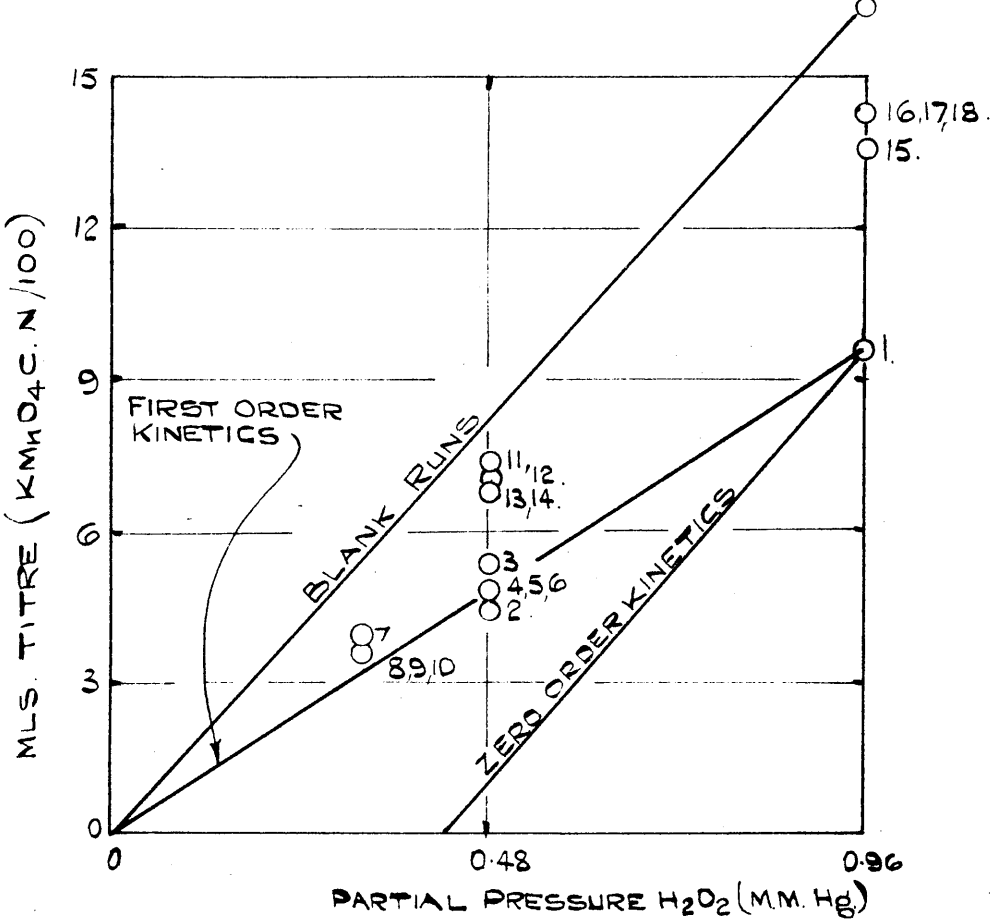
| Oxide | Temperature Change (°C) | | % Decomposition | | Activation Energy (K.cals/mol) |
|---|---|---|---|---|---|
| | $T_1$ | $T_2$ | $T_1$ | $T_2$ | |
| CdO | 100 | 183 | 32 | 87.5 | 10.8 |
| CdO | 183 | 138 | 80.1 | 42.2 | 11.4 |
| $Fe_2O_3$ | 138 | 100 | 80.0 | 25.7 | 22.0 |
| $Fe_2O_3$ | 100 | 78 | 37.1 | 0 | - |
| CuO | 101 | 130 | 50.9 | 95.2 | 16.5 |
| CuO | 130 | 77 | 82.1 | 8.0 | 18.4 |

Reaction order.

The order of the decomposition was studied on all four oxides and showed little or no deviation from first order behaviour on lowering the concentration from Ci to Ci/2 etc. However, on making a change Ci/3 → Ci/2 → Ci, all the catalysts deactivated markedly, a phenomena which was not apparent with the class (1) oxides. In the special case of ZnO, the catalyst showed almost complete deactivation even on making the original Ci to Ci/2 concentration change. These points are illustrated in Fig. 32.

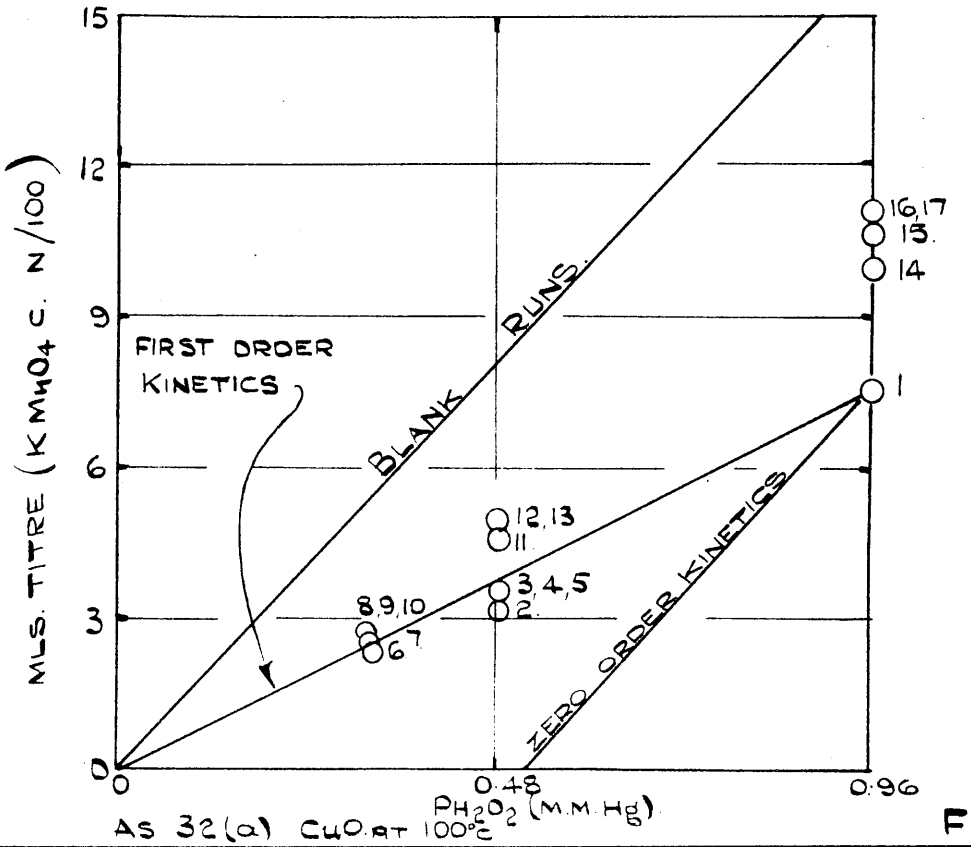
(e) Class (3)

This comprises the inactive oxides MgO and $\alpha$-$Al_2O_3$. Neither of these were catalytically active at 183°C when used as the freshly prepared




DETERMINATION OF KINETICS ON $Fe_2O_3$ AT 100°C.
SHOWING LOSS OF ACTIVITY ON RESTORING Ci.
POINTS AT 5 MINUTE INTERVALS

FIG. 32 (a)




AS 32(a) CuO AT 100°C

FIG. 32(b)

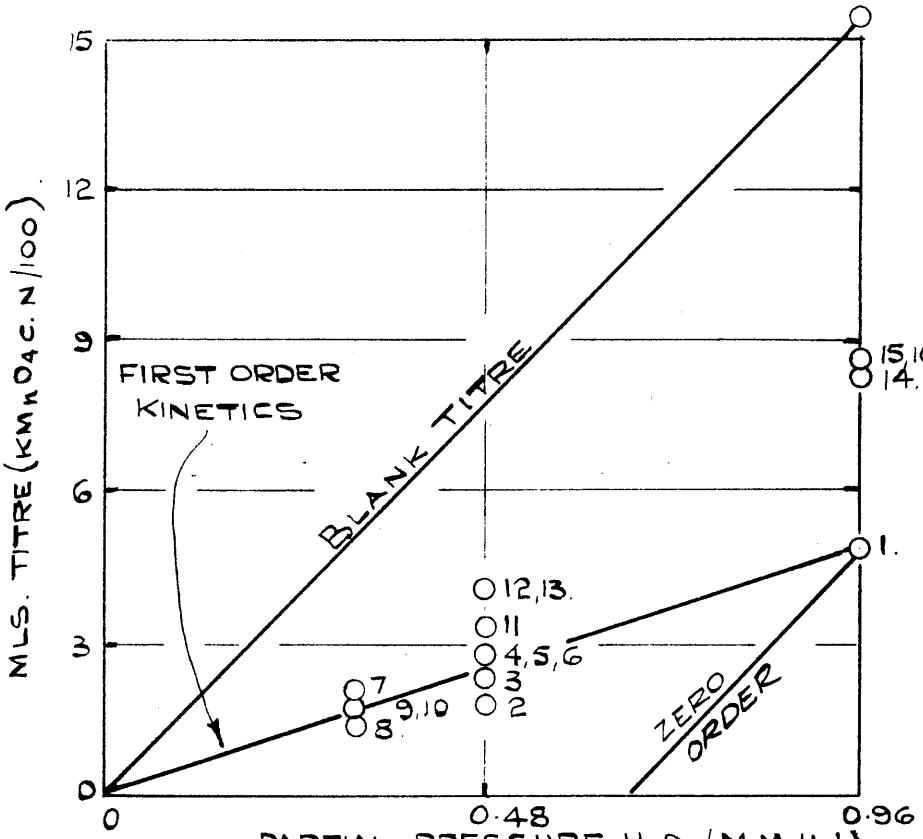
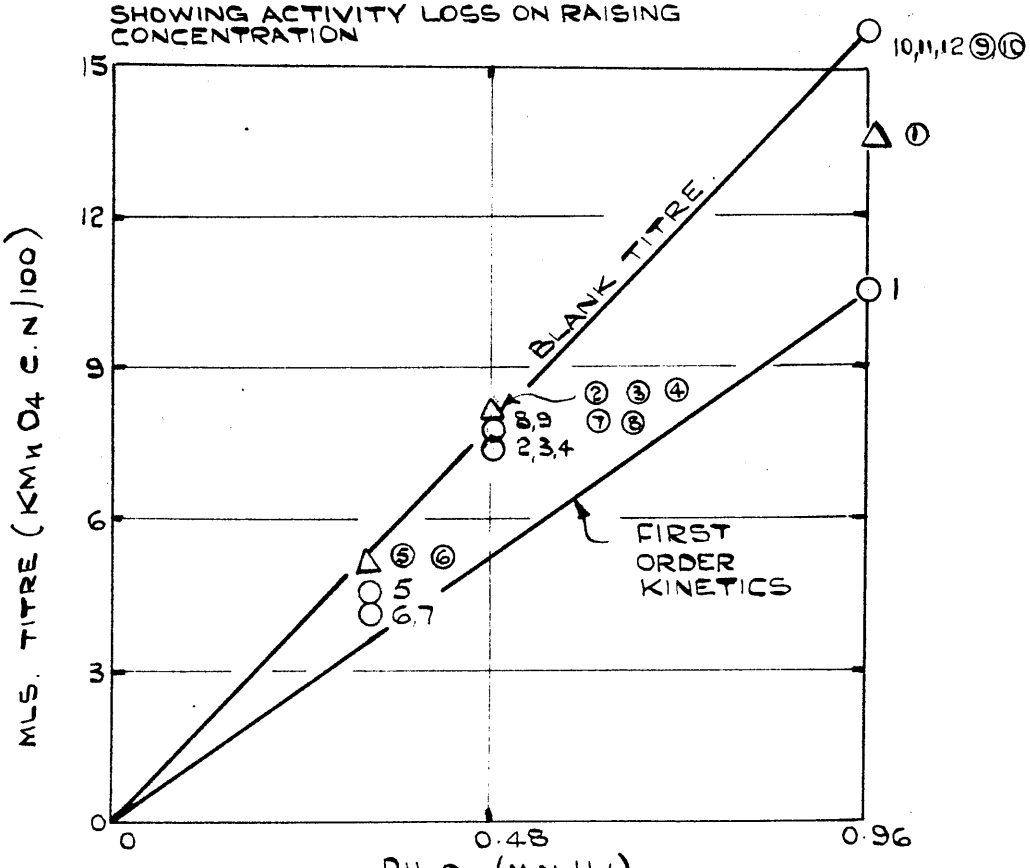



FIG 32 (c.)

DETERMINATION OF KINETICS ON CdO. AT 183°c.
SHOWING ACTIVITY LOSS ON RAISING CONCENTRATION




DETERIORATION OF ZnO IN CONCENTRATION CHANGES

Δ – 100°c ; ○-138°c.

FIG 32 (d).

slips. However, they did become slightly active after prolonged (10 hours) heat treatment at 900-1000°C in a mullite tubular furnace in air. (It is necessary to emphasise that the oxides were fired separately in mullite boats, in a furnace with a fresh lining in order to avoid contamination through impurities from previous calcinations "creeping" over the oxides).

Alumina, heat-treated in this way, would form $\alpha$-$Al_2O_3$ (102). It was active for a short time in decomposing a steady fraction of peroxide vapour but became ineffective when the concentration was raised to a higher value, e.g. 0.44 mm. to 0.88 mm. Hg. The kinetics could not be determined because of this behaviour.

The catalytic efficiency of $\alpha$ - $Al_2O_3$, unlike $Al/Al_2O_3$ (activated), showed an almost linear decline in time. For example, an initial decomposition of 37.5% at 140°C (0.88 mm. Hg, p.p. $H_2O_2$) would fall to zero within 50 minutes. The following table illustrates this.

TABLE 23. Deterioration of $\alpha$ - $Al_2O_3$, at various $H_2O_2$ concentrations.

| Reaction Temperature (°C) | $H_2O_2$ partial pressure (mm.Hg) | Initial Decomposition | Time to zero decomposition (Mins) |
|---|---|---|---|
| 140 | 0.96 | 33.5% | 45 |
| 183 | 0.25 | 48.9% | 30 |
| 140 | 1.01 | 35.0% | 40 |
| 100 | 0.96 | 10.0% | 35 |

Refractory magnesium oxide when subjected to the same heat treatment, gave no detectable activity until 183°C. At this temperature decompositions between 43 and 45% were recorded with three separate specimens, which in

75 minutes had fallen to a value of 38 - 39%.

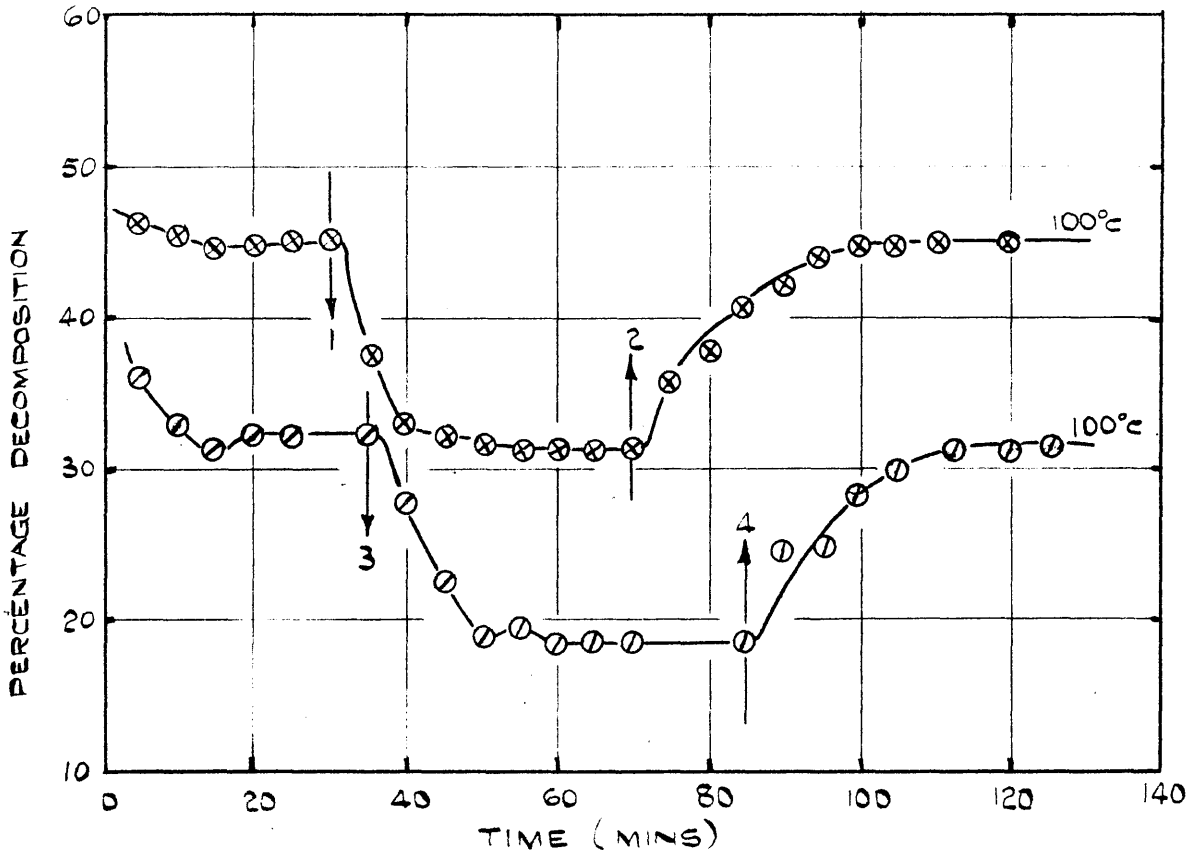
The kinetics of the reaction on MgO were determined at 183°C for concentration changes from $C_i$ (p.p.$H_2O_2$ = 0.88 mm Hg) to $C_i/2$ to $C_i/3$, the reverse procedure giving almost immediate inactivation of the catalyst as is shown in Table 24.

TABLE 24. Determination of Reaction order on MgO, heat treated at 1000°C for 10 hours, at 183°C.

| $H_2O_2$ partial pressure (mm. Hg) | Percentage Decomposition | Time from initial exposure to $H_2O_2$ vapour (mins.) | Remarks |
|---|---|---|---|
| 0.88 | 43.1 | 5 | |
| 0.88 | 42.8 | 10 | First order kinetics |
| 0.44 | 42.2 | 15 | |
| 0.44 | 42.1 | 20 | First order kinetics |
| 0.29 | 41.7 | 25 | |
| 0.29 | 41.7 | 30 | |
| 0.44 | 4.3 | 35 | Deactivation |
| 0.44 | 0.0 | 40 | No decomposition |
| 0.88 | 0.0 | 45 | " |

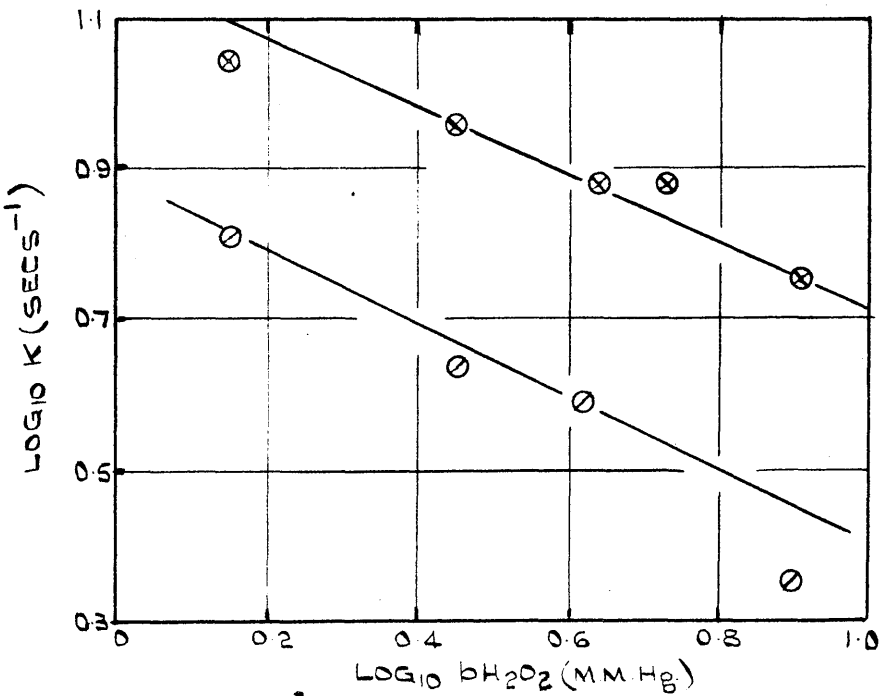
As the table shows, the concentration changes $C_i$ to $C_i/2$ and $C_i/2$ to $C_i/3$ make no alteration to the fraction of $H_2O_2$ vapour decomposed (apart that is, from a small efficiency decrease, considered to be due to slow catalyst de-activation), and the kinetics are first order with respect to $H_2O_2$ concentration in each change.

(f) Influence of oxygen and water vapour on bulk oxide catalysis.




EFFECT OF $H_2O$ VAPOUR ON REACTION RATE. SHOWING PATTERN OF RATE CHANGES p.p $H_2O_2$ = 0.48 MM Hg
⊗ "GREEN" NiO (pp $H_2O$ = 5.37 MM Hg.)
⊘ $Fe_2O_3$ (pp $H_2O$ = 4.17 M.M. Hg.)
$H_2O$ ADDED AT POINTS 1 & 3, REMOVED AT 2 & 4.

FIG. 33(a)




VARIATION OF RATE CONSTANT WITH $pH_2O$.
⊗ "GREEN" NiO. (100°c) ⊘ $Fe_2O_3$ (100°c)

FIG. 33(b)

The effect of added oxygen and water vapour on the catalysis was examined on $Fe_2O_3$, "green" NiO and $\alpha$-$Al_2O_3$. The influence of water vapour on the reaction proceeding on the first two oxides is shown in Table 25 below.

TABLE 25. Influence of water vapour on reaction rate. "Green" NiO and $Fe_2O_3$ catalysts. Partial pressure $H_2O_2$ = 0.48 mm Hg.

| Catalyst | Temperature of Run (°C) | Steady Decomposition (%) No $H_2O$ added. | Partial pressure $H_2O$ after addition (mm Hg). | Steady Decomposition (%) with added $H_2O$ |
|---|---|---|---|---|
| NiO | 100 | 45.7 | 8.13 | 24.9 |
| " | " | 45.2 | 5.37 | 31.4 |
| " | " | 45.2 | 4.37 | 31.5 |
| " | " | 44.7 | 2.82 | 36.5 |
| " | " | 45.1 | 1.41. | 42.0 |
| $Fe_2O_3$ | 100 | 31.8 | 7.94 | 10.8 |
| " | " | 32.4 | 4.17 | 18.1 |
| " | " | 32.0 | 2.82 | 19.5 |
| " | " | 31.9 | 1.41 | 27.2 |

The value of $pH_2O$ given in column 4 above refers to the partial pressure of $H_2O$ added plus that produced in the decomposition.

On $\alpha$-$Al_2O_3$ the reaction was immediately poisoned on adding $H_2O$ vapour of partial pressures 3 - 4 mm Hg, and no reaction was recorded at 183°C. Fig. 33(a) shows the general pattern of rate changes found with water vapour additions, and Fig. 33(b) shows the variation induced in the rate constant from which it can be seen that, as with the metal/oxide catalysts:-

$$\text{Rate} \propto (pH_2O)^{-\frac{1}{2}}$$

The influence of oxygen on the reaction velocity was again determined by finding the steady decomposition level given by a catalyst with only the oxygen produced in the decomposition, and that with the inert carrier gas replaced totally by oxygen. The results are shown in Table 26.

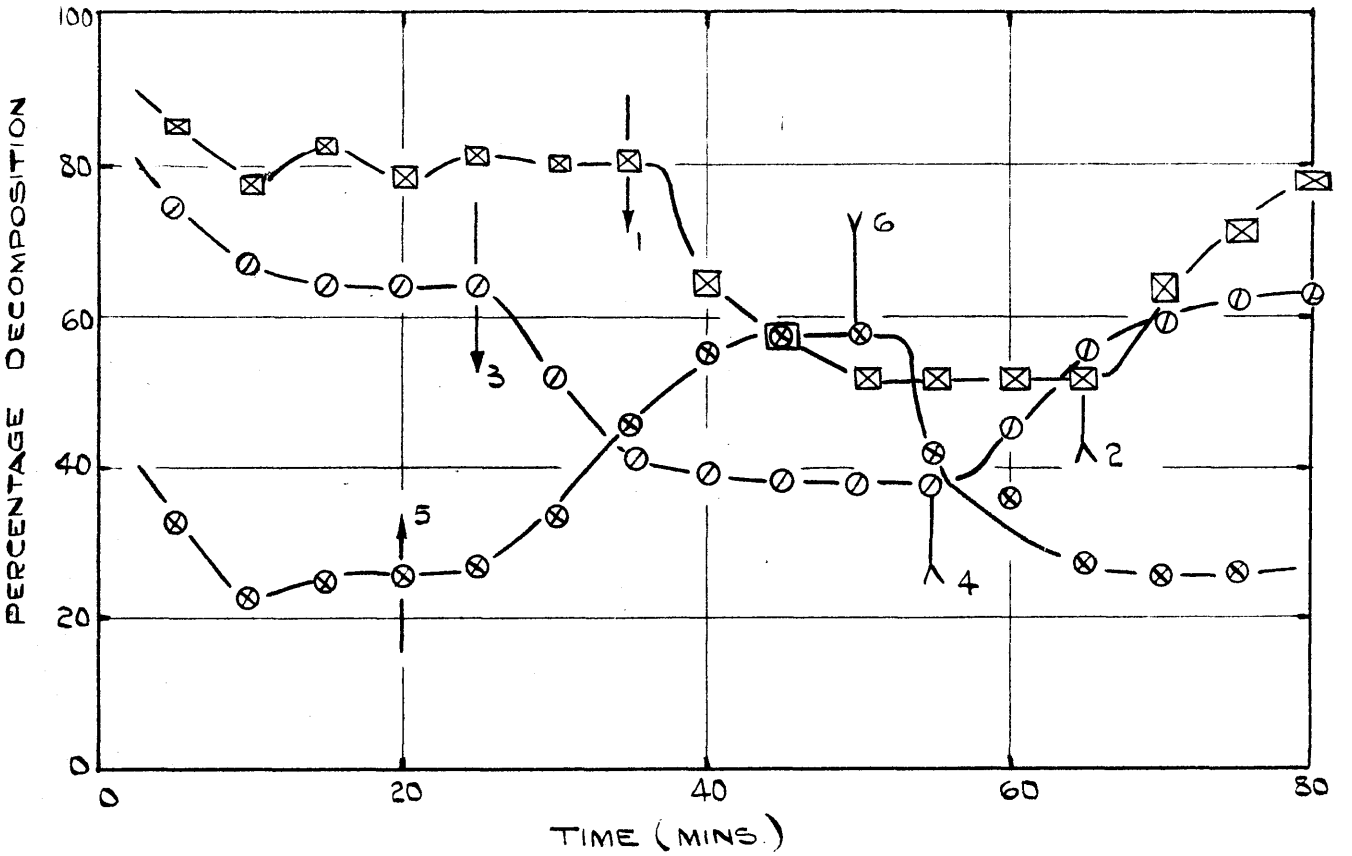
TABLE 26. Effect on steady decomposition of replacement of nitrogen by oxygen as the carrier gas.
($p.p.H_2O_2$ = 0.96 mm. Hg).

| Catalyst | Temperature of Run (°C) | Steady Decomposition (%) $N_2$ carrier. | Steady Decomposition (%) carrier. |
|---|---|---|---|
| NiO | 60 | 26.4 | 57.0 |
| NiO | 100 | 50.1 | 80.9 |
| $Fe_2O_3$ | 100 | 38.0 | 64.1 |

On $\alpha - Al_2O_3$, the influence of oxygen was only just apparent, in that, the decomposition at 183°C was raised from 50% to 52-53% on first addition, but the deactivation continued on the same course as that shown in Table 23. With "black" NiO, whilst addition of oxygen accelerated the decomposition, it did not effectively alter the speed of the colour change black to green, by visual observation. This still took about 100-120 mins. at 100°C to become a murky green.

Fig. 34(a) shows the influence of oxygen on the decomposition pattern, and 34(b) the variation of the rate constant, in which the lines are drawn to form a parallel series showing that:-

$$\text{Rate} \propto (pO_2)^{1/8}$$



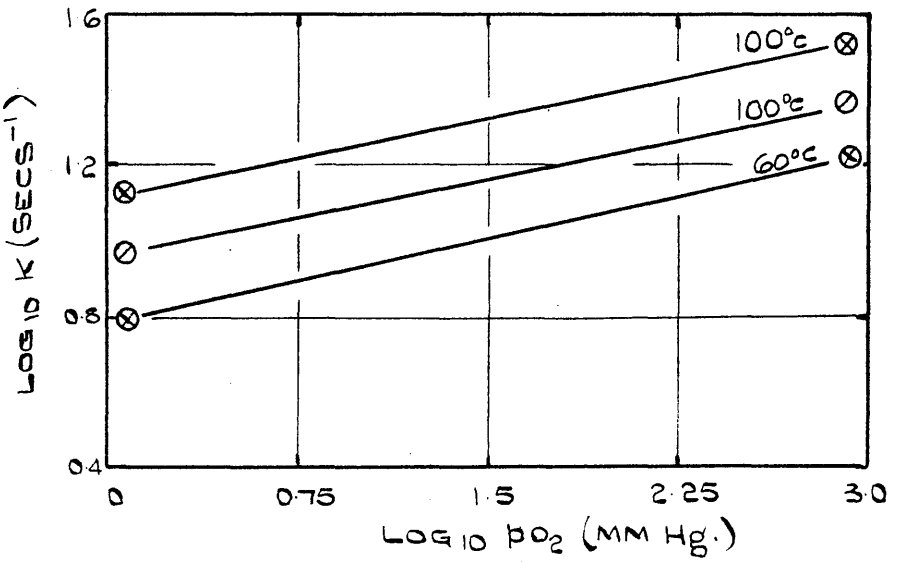

INFLUENCE OF OXYGEN ON DECOMPOSITION PATTERN.

⊠ "GREEN" NiO (AT 100°C) ⊗ "GREEN" NiO (60°C) ⊘ $Fe_2O_3$ (100°C)

POINTS 1,3,6 OXYGEN CARRIER GAS → NITROGEN CARRIER GAS

" 2,4,5 NITROGEN " " → OXYGEN " "

FIG. 34(a.)




EFFECT ON CATALYSIS RATE, OF REPLACEMENT OF $N_2$ by $O_2$ AS THE CARRIER GAS

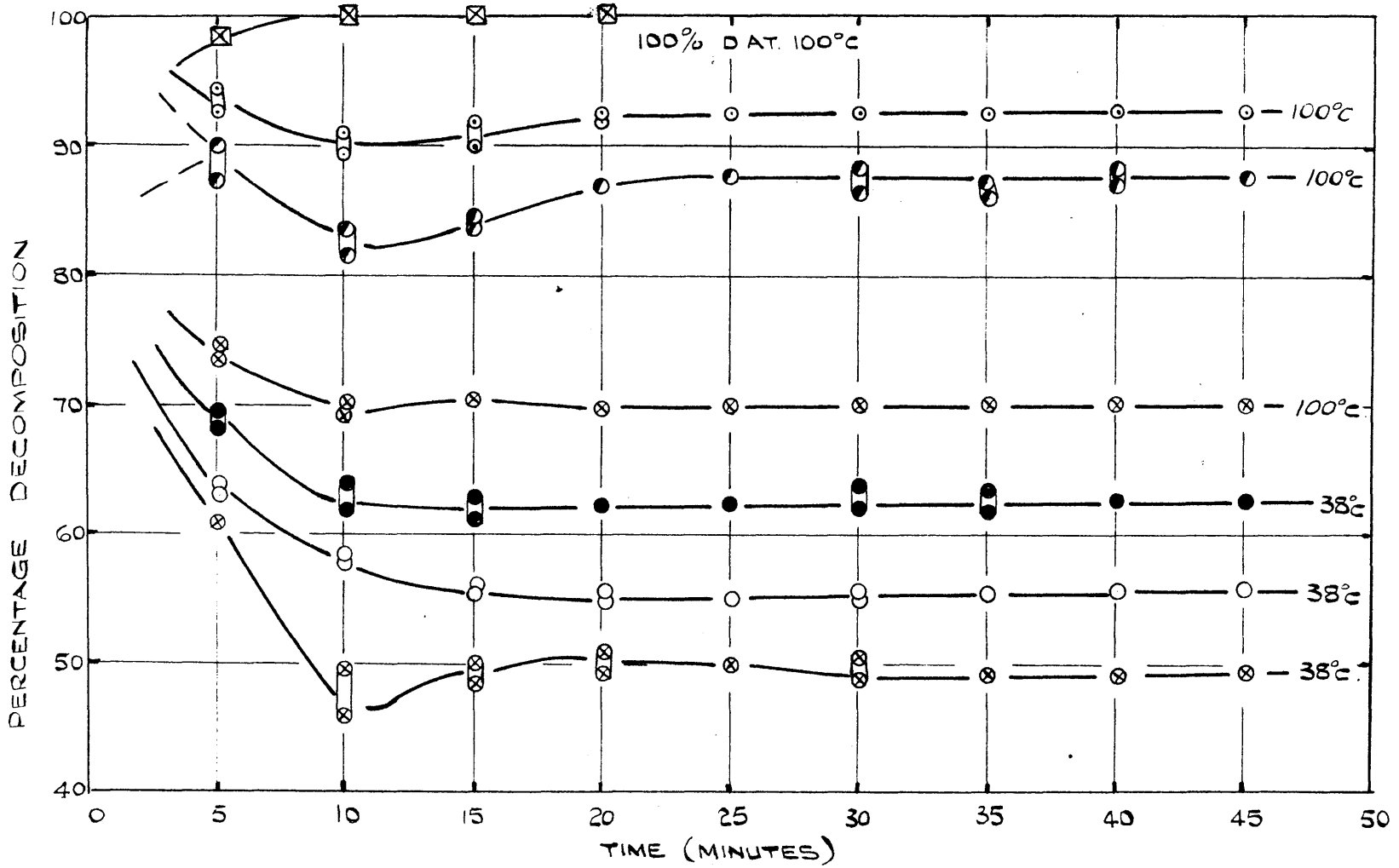
⊗ "GREEN" NiO ⊘ $Fe_2O_3$

FIG. 34(b.)

It is possible that further data would yield better values for this gradient, but it appears fairly certain to lie in the region 1/6 - 1/10.

It may be concluded that the over-all reaction rate on NiO and $Fe_2O_3$ may be represented by a similar expression as found for certain metal/ oxides, viz:-

$$\text{Rate} \propto K. \frac{(pH_2O_2)\ (pO_2)^{1/8}}{(pH_2O)^{\frac{1}{2}}}$$




EFFICIENCY CHANGES ON EQUI-MOLAR MIXED OXIDES ON FIRST EXPOSURE SHOWING REPRODUCIBILITY OF INITIAL TREND

- ● $ZnO/Mn_2O_3$ (400°C. PREPARATION.)
- ◐ $CdO/Mn_2O_3$ (600°C.)
- ⊙ $PbO/Mn_2O_3$ (400°C)
- ○ $NiO/Mn_2O_3$ (720°C.)
- ⊗ $ZnO/Mn_2O_3$ (760°C)
- ⊠ $PbO/Mn_2O_3$ (600°C.)

FIG. 35

(4) Equimolar oxide mixtures.

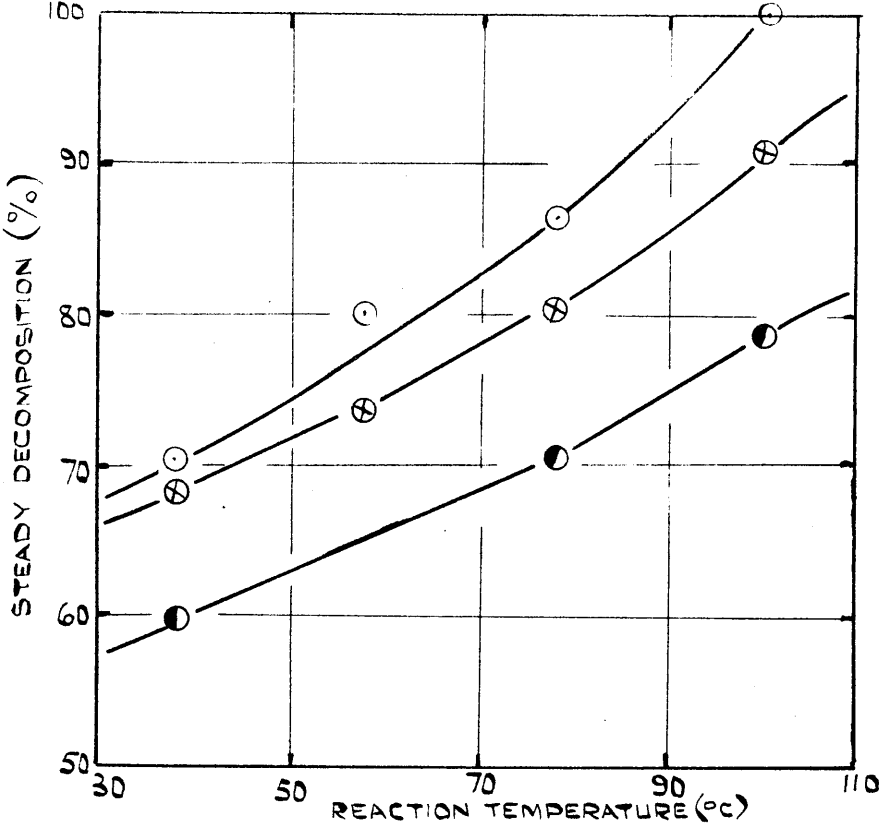
In this section the study of the vapour phase decomposition of $H_2O_2$ by highly catalytic materials is extended to include a detailed survey of certain mixed oxides of the type $XO.Y_2O_3$. In one series the trivalent oxide used was $Mn_2O_3$ to which equimolar additions of PbO, ZnO and NiO were separately added by a mechanical mixing and grinding procedure. The resulting mixtures were fired at controlled temperatures in an inert atmosphere for six hours.

In another series the divalent oxide was fixed as CuO and equimolar additions of $Fe_2O_3$, $\alpha$-$Al_2O_3$ and $Co_2O_3$ were made by the same procedure as outlined above. The heat treatment in this case was carried out in air for six hours.

(a) Catalytic activity - $Mn_2O_3$ series.

The series based on $Mn_2O_3$ proved to be highly active. The temperature for 50% decomposition was as low as 30-40°C for all the oxides examined. The catalytic activity was studied in the range 38 - 100°C and did not show a high temperature dependance. Fig. 35 illustrates the attainment of steady decomposition levels at different temperatures. It can be seen that the various catalyst surfaces exhibit an irregularity in behaviour before leveling out. This behaviour on starting up was easily reproducible for each catalyst surface in fresh runs at the same $H_2O_2$ concentration as the figure illustrates.

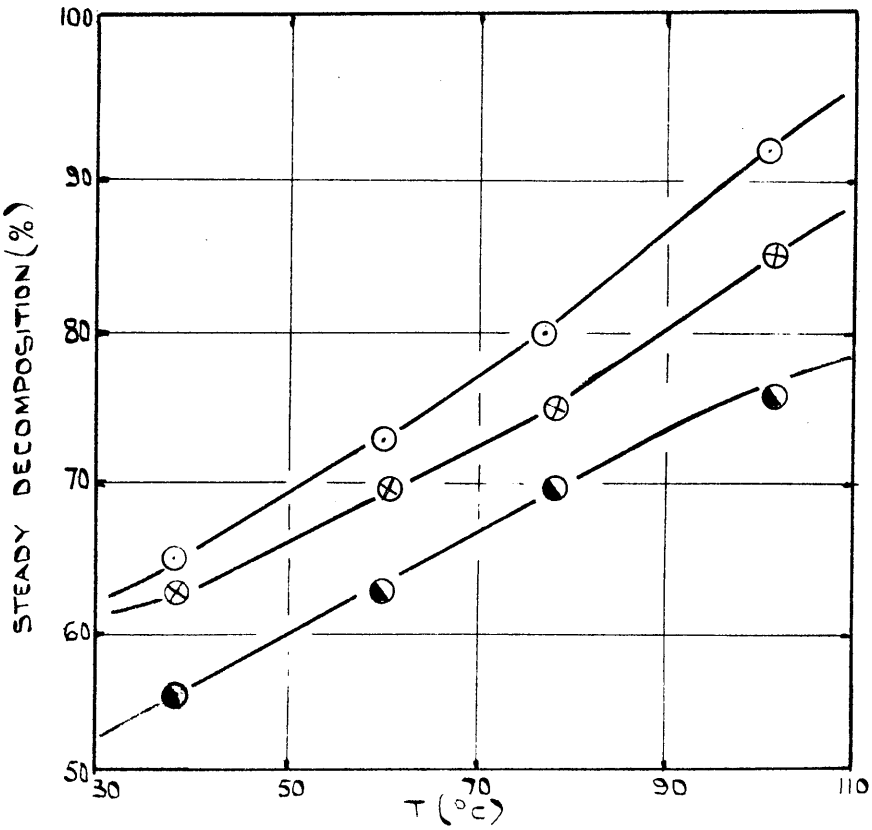
The influence of temperature of preparation was also studied for the $Mn_2O_3$ mixtures and the results are shown in Figs. 36(a), (b), (c), in which the steady level of catalysis is plotted against the temperature of the run. This is given for each mixed oxide pre-fired at the temperatures shown in




VARIATION OF ACTIVITY WITH TEMPERATURE OF PRETREATMENT

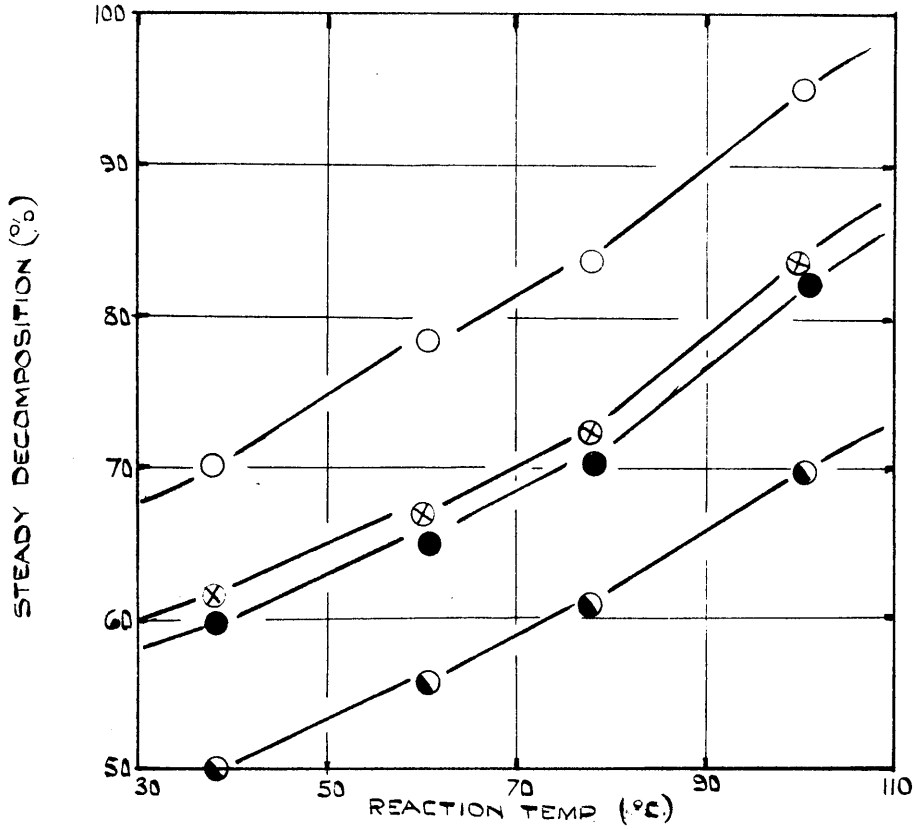
$PbO/Mn_2O_3$ : ⊙ – 600°C PREPN.
⊗ – 400°C "
◐ – 760°C "

FIG. 36(a)



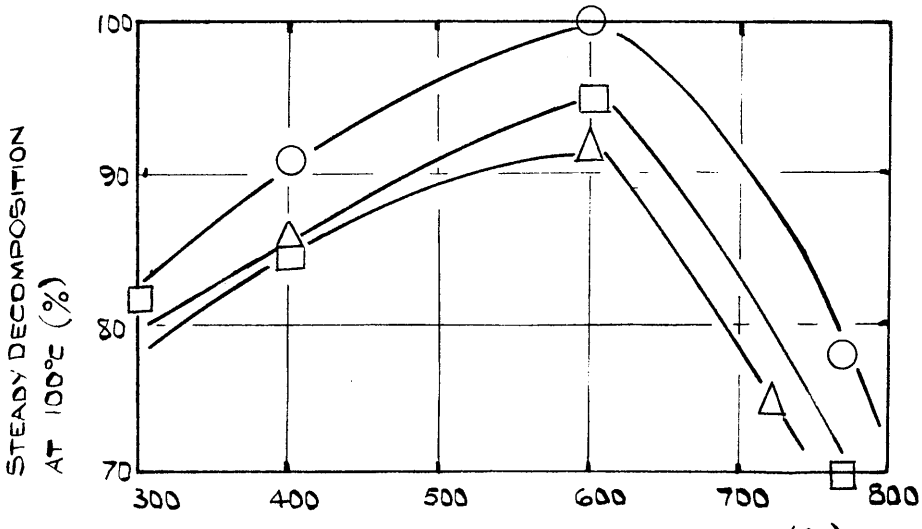

LEGEND AS 36(a) ; $NiO/Mn_2O_3$ CATALYST
⊙ 600°C ⊗ 400°C ◐ 720°C

FIG. 36(b)




VARIATION OF ACTIVITY WITH TEMPERATURE OF PRETREATMENT $ZnO/Mn_2O_3$ ⊙ 600°C PREPERATION.
⊗ 400°C "
● 300°C "
◐ 760°C "

FIG. 36(c).




PEAK ACTIVITY CURVES
○ $PbO/Mn_2O_3$
□ $ZnO/Mn_2O_2$
△ $NiO/Mn_2O_3$

FIG. 37.

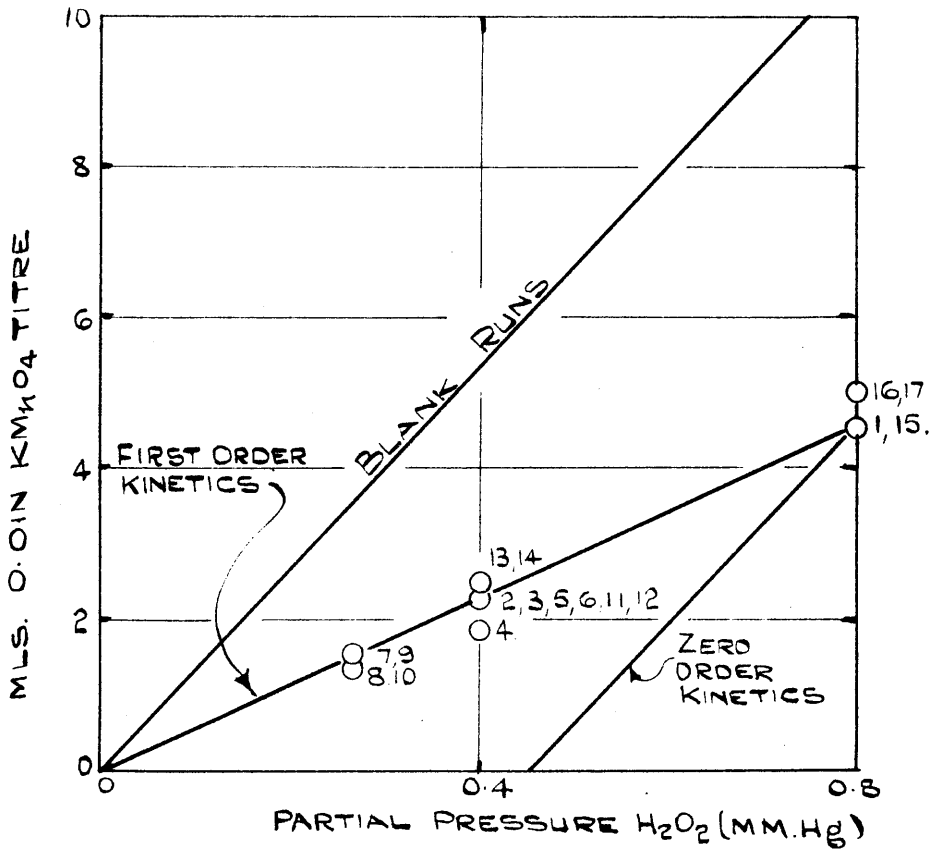
the graph legend. The figures show that the mixtures were all very active. The best catalysts were the $PbO/Mn_2O_3$ series in which the single oxides alone are of a high efficiency, as has been shown earlier in this section. The $Mn_2O_3$ mixtures with ZnO and NiO appeared to be equally active at the same temperature. The graphs show that the samples prepared at 600°C were the most active catalysts in all three instances. The preparations carried out at 300°C showed little or no difference in activity from that of the 400°C preparations, whilst the mixtures pre-fired at 720 or 760°C were, in all three cases, the least efficient. This is illustrated in Fig. 37 where the steady decomposition at 100°C is plotted against the preparation temperature of the catalyst for the three series. (It should be noted here that the mixtures were all ground to pass 300 B.S. sieve after firing in mullite boats and before compressing into slips).

Kinetic order.

The kinetics of the decomposition reaction were examined on the following three selected specimens:- $NiO/Mn_2O_3$ (prepared at 400°C); $ZnO/Mn_2O_3$ (300°C) and $PbO/Mn_2O_3$ (600°C). The results are illustrated in Figs. 38(a), (b), (c), (d). The numbered points refer to consecutive five minute runs at three different (0.80, 0.40, 0.27 mm. Hg) peroxide partial pressures at a total constant flow of 300 mls of vapour per minute. In the course of each experiment lasting about two hours there was a very slight activity loss with all the catalysts shown when the initial $C_i$ value was restored at the end of each run. Allowing for this first order kinetics were observed in all cases.

Temperature coefficient.

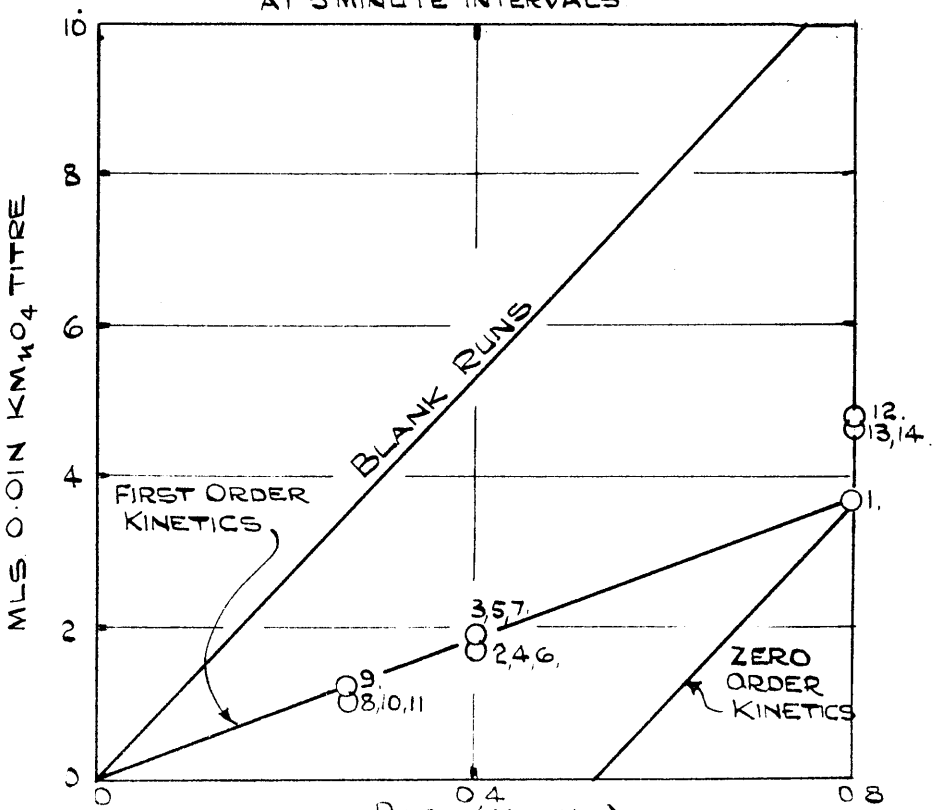
The determination of the temperature coefficient of the efficiency




DETERMINATION OF REACTION ORDER. ZnO/Mn2O3 (300°C PREPARATION) AT 60°C

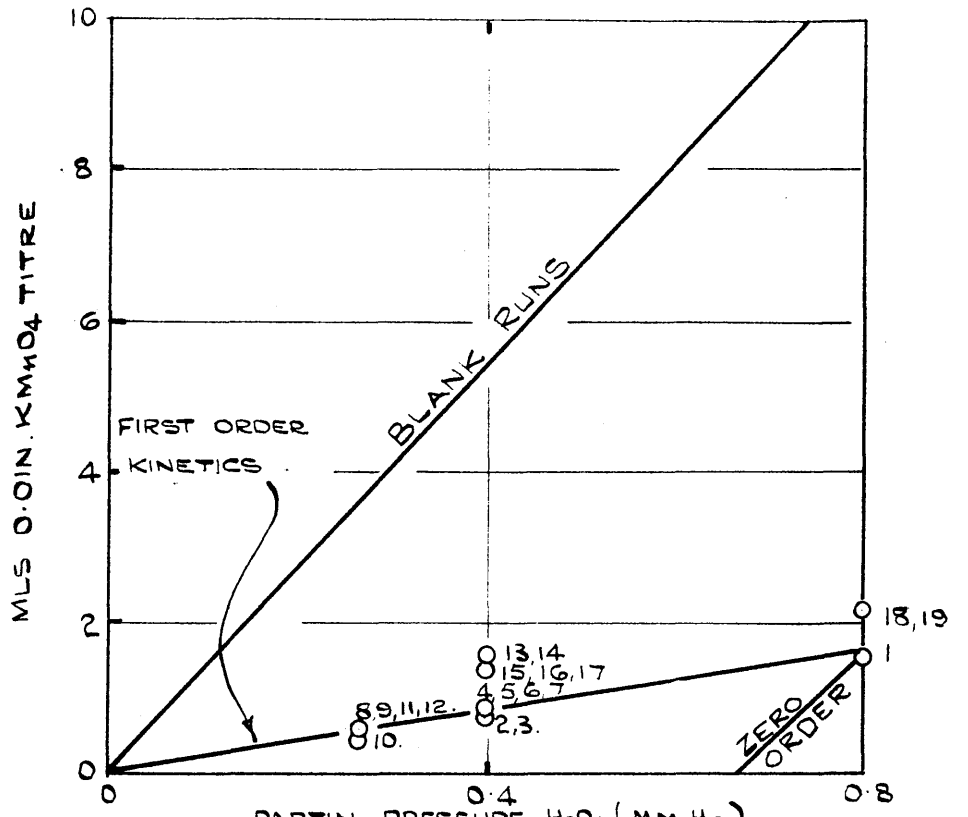
POINTS NUMBERED IN EXPERIMENTAL SEQUENCE AT 3 MINUTE INTERVALS

FIG. 38 (a)



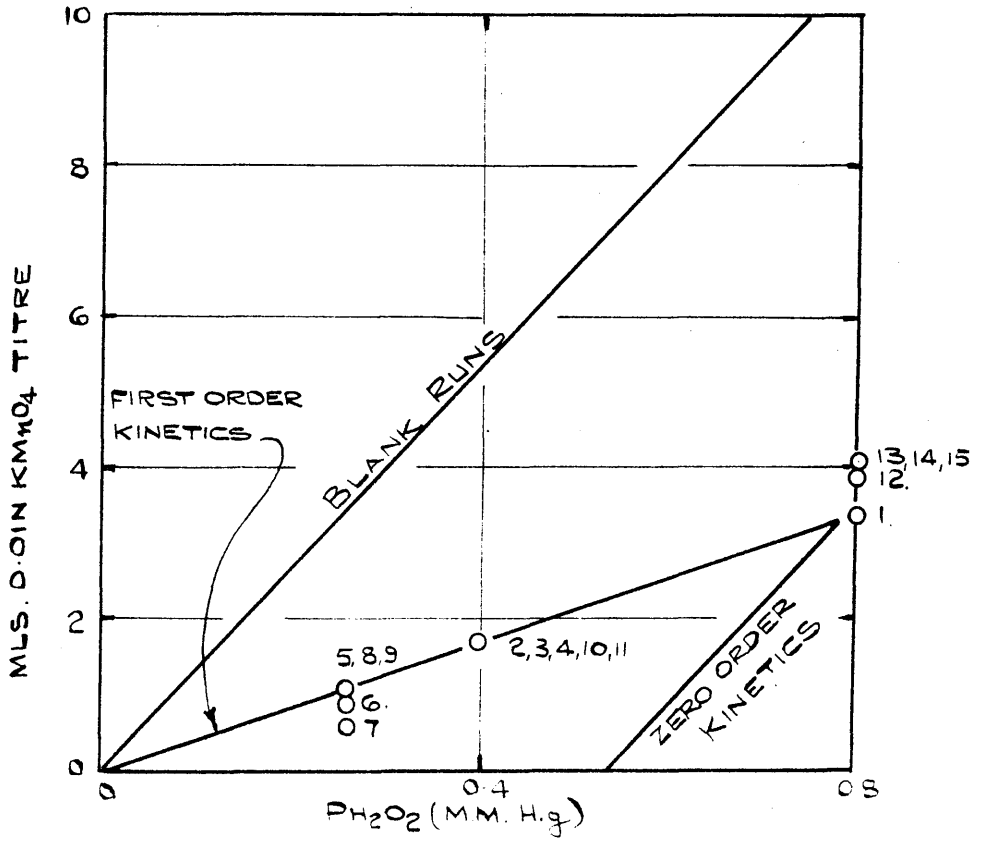

AS 38 (a) TEMPERATURE = 77·5°C.

FIG 38 (b)




DETERMINATION OF REACTION ORDER ON $NiO/Mn_2O_3$ (400° PREPARATION) AT 100°C
POINTS AT 5 MINUTE INTERVALS.

FIG. 38(c)




DETERMINATION OF REACTION ORDER ON $PbO/Mn_2O_3$ (600°C PREPARATION) AT 38°C
POINTS AT 5 MINUTE INTERVALS

FIG. 38(d)

was made by making rapid temperature changes in the region 38 - 100°C. The results are tabulated below for runs at a constant $H_2O_2$ partial pressure (0.88 mm. Hg). The stepwise changes being in the sequence 77°C $\longrightarrow$ 60°C $\longrightarrow$ 100°C $\longrightarrow$ 39°C.

TABLE 27. Temperature coefficients $XO/Mn_2O_3$ series.

| Oxide | Preparation Temperature (°C) | Temperature Change (°C) | | Activity Change (%) | | Activation Energy (K.cals/mol) |
|---|---|---|---|---|---|---|
| | | 77 | 60 | 78 | 64 | 5.4 |
| $PbO/Mn_2O_3$ | 300 | 60 | 100 | 68 | 90 | 4.8 |
| | | 100 | 39 | 87 | 60 | 3.1 |
| | | 78 | 59.5 | 80 | 64 | 5.7 |
| $PbO/Mn_2O_3$ | 400 | 59.5 | 100.5 | 68 | 95 | 5.9 |
| | | 100.5 | 38 | 90 | 55 | 4.1 |
| | | 77 | 59.5 | 86 | 70 | 5.4 |
| $PbO/Mn_2O_3$ | 600 | 59.5 | 100 | 78 | 97 | 5.3 |
| | | 100 | 39 | 93 | 55 | 4.7 |
| | | 77 | 60 | 72 | 64 | 3.2 |
| $NiO/Mn_2O_3$ | 300 | 60 | 100 | 70 | 90 | 4.3 |
| | | 100 | 38 | 84 | 58 | 3.0 |
| | | 76 | 60 | 74 | 61 | 4.1 |
| $NiO/Mn_2O_3$ | 400 | 60 | 100 | 67 | 93 | 5.1 |
| | | 100 | 39 | 89 | 58 | 3.8 |

TABLE 27. (Continued).

| Oxide | Preparation Temperature (°C) | Temperature Change (°C) | | Activity Change (%) | | Activation Energy (K.cals/mol) |
|---|---|---|---|---|---|---|
| | | 76 | 60 | 80 | 69 | 5.0 |
| $NiO/Mn_2O_3$ | 600 | 60 | 100 | 72 | 95 | 4.5 |
| | | 100 | 38 | 90 | 57 | 4.0 |
| | | 78 | 60 | 69 | 56 | 5.1 |
| $NiO/Mn_2O_3$ | 720 | 60 | 100 | 61 | 85 | 4.4 |
| | | 100 | 38 | 80 | 42 | 4.5 |
| | | 78 | 58 | 83 | 71 | 4.2 |
| $ZnO/Mn_2O_3$ | 600 | 58 | 100 | 76 | 98 | 5.9 |
| | | 100 | 39 | 94 | 63 | 4.0 |
| | | 78 | 59 | 69 | 51 | 5.9 |
| $ZnO/Mn_2O_3$ | 760 | 59 | 100 | 55 | 78 | 3.7 |
| | | 100 | 38 | 74 | 43 | 3.4 |
| | | 77 | 60 | 83 | 69 | 4.4 |
| $CdO/Mn_2O_3$ | 600 | 60 | 100 | 73 | 97 | 6.2 |
| | | 100 | 38 | 94 | 62 | 4.0 |

The differences in the $E_A$ values are often not significant since they lie within the range $\pm$ 1 K.cal which is all that can be claimed for the reproducibility of this value. There is, however, a systematic tendency for the value obtained from 100°C to be lower than the others.

This is in opposition to what was normally found with pure oxides.

In view of the closeness of these three values, averages have been taken and are recorded in Table 27(a).

TABLE 27(a). Average $E_A$ values $XO/Mn_2O_3$ series.

| Oxide | Preparation Temperature (°C) | Mean Activation Energy (K.cals/mol). |
|---|---|---|
| $PbO/Mn_2O_3$ | 300 | 4.4 |
| " | 400 | 5.2 |
| " | 600 | 5.1 |
| $NiO/Mn_2O_3$ | 300 | 3.5 |
| " | 400 | 4.3 |
| " | 600 | 4.5 |
| " | 720 | 4.7 |
| $ZnO/Mn_2O_3$ | 300 | 4.0 |
| " | 600 | 4.7 |
| " | 760 | 4.3 |
| $CdO/Mn_2O_3$ | 600 | 4.8 |

It can be seen from the above data that the activation energy seems to increase as the catalyst activity decreases. The temperature coefficient increases slightly with increasing sintering temperature, analogous to the behaviour of $Mn_2O_3$ itself, which is of such a high catalytic power that an equimolar addition of an inactive oxide (ZnO) did not cause any marked deterioration in activity. Similarly, the addition of active oxides (NiO, PbO) improved the activity by only a few percent.

(b) Catalytic activity:- CuO series.

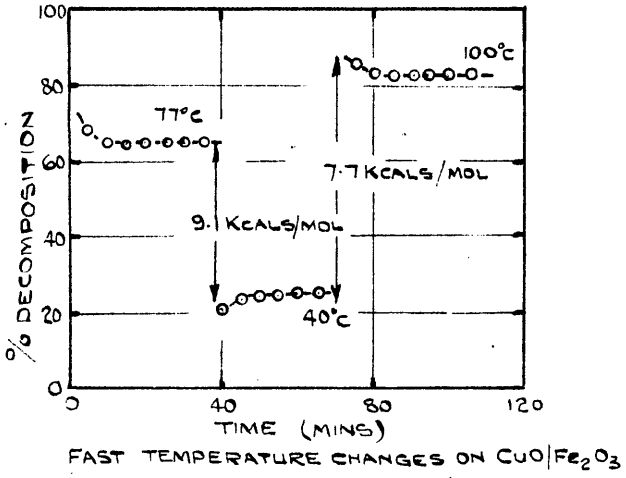
This series consisted of the mixtures $CuO/Fe_2O_3$, $CuO/Al_2O_3$ and $CuO/Co_2O_3$. Apart from the latter they were less active than the $Mn_2O_3$ series.

Figs. 39 (a), (b) and (c) show the course of the catalytic efficiency in making fast temperature changes on all three materials to obtain the experimental activation energies, which are given in Table 28 below.

TABLE 28. Experimental activation energies $CuO/Y_2O_3$ series, prepared at 600°C in air.

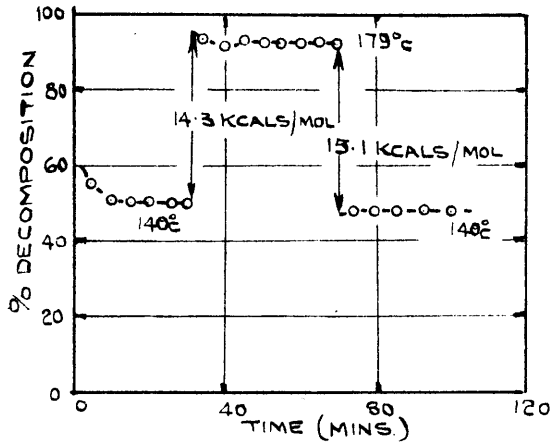
| Oxide | Temperature Change (°C) | | Activity Change (%) | | Activation Energy (K.cals/mol) |
|---|---|---|---|---|---|
| $CuO,Fe_2O_3$ | 77 | 40 | 65 | 20 | 9.1 |
| $CuO.Fe_2O_3$ | 40 | 100 | 25 | 87 | 7.7 |
| $CuO.Al_2O_3$ | 140 | 179 | 50 | 95 | 14.3 |
| $CuO.Al_2O_3$ | 179 | 140 | 93 | 48 | 15.1 |
| $CuO.Co_2O_3$ | 100 | 39 | 80 | 45 | 4.2 |
| " | 39 | 77 | 48 | 75 | 3.7 |

As Table 25 shows an equimolar mixture of CuO and $Fe_2O_3$ was much more active than these as single oxides, which had to be studied in the 100-183°C temperature range. The effect was also to decrease markedly the activation energy required by CuO (15 K.cals/mol) and $Fe_2O_3$ (20K.cals/mol). The most inactive mixture was CuO. $Al_2O_3$ which only showed appreciable activity at temperatures > 100°C and gave a similar activation energy to that of CuO.



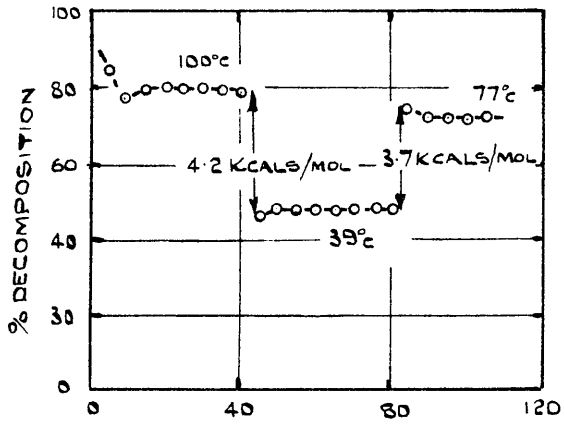

FAST TEMPERATURE CHANGES ON $CuO|Fe_2O_3$

FIG 39(a)




FAST TEMPERATURECHANGES ON $CuO/Al_2O_3$

FIG. 39(b)




FAST TEMPERATURE CHANGES ON $CuO/Co_2O_3$

FIG. 39(c)

(c) Magnetic susceptibility results.

The magnetic susceptibility measurements showed a striking correspondence between X and the temperature of preparation of the series $AO/Mn_2O_3$. Thus, for the system $PbO/Mn_2O_3$, the susceptibility tends to decrease with increasing temperature but finally reaches a steady value. $ZnO/Mn_2O_3$ falls to approximately the same value for the specimen sintered at 760°C but tends to this level suddenly after a progressive increase of X. On the other hand, the system $NiO/Mn_2O_3$ shows preliminary changes before 600°C is reached and then shoots into the zone of ferromagnetism. The results are given in Table 29 and are indicative of structural changes during progressive sintering.

TABLE 29. Magnetic susceptibilities $AO/Mn_2O_3$ series at 20°C. (Infinite field).

| Mixed Oxide | X x $10^6$ (c.g.s. units). | | | | |
|---|---|---|---|---|---|
| | 300°C | 400°C | 500°C | 600°C | 760°C |
| $PbO/Mn_2O_3$ | 73.9 | 72.2 | 19.5 | 19.6 | - |
| $NiO/Mn_2O_3$ | 89.6 | 95.2 | 109.2 | Ferro-magnetic | Ferro-magnetic |
| $ZnO/Mn_2O_3$ | 79.3 | 80.2 | 83.0 | 104.0 | 35.6 |
| * $ZnO/Mn_2O_3$ | 75.1 | 74.5 | 79.2 | 97.4 | - |

* These mixtures were examined after exposure to $H_2O_2$ vapour for two hours at 150°C, (flow rate = 300 mls/min; $pH_2O_2$ = 0.88 mm Hg). There was a marked tendency for the susceptibility of the oxide mixture to decrease in each case after being used in the catalysis. The effect may be related to a change in oxidation state of the catalyst surface through a partial

reduction by the action of the hydrogen peroxide.

The susceptibility results obtained for the $CuO/Fe_2O_3$ mixtures are given in Table 30 found from extrapolations to $1/H = 0$.

TABLE 30. Magnetic susceptibilities $CuO/Y_2O_3$ series at 20°C.

(Infinite field strength)

| Oxide | Magnetic Susceptibility (cgs. units) | |
|---|---|---|
| | Room Temperature | Sintered (600°C). |
| CuO | $2.88 \times 10^{-6}$ | $2.85 \times 10^{-6}$ |
| $\alpha$- $Fe_2O_3$ | $22.00 \times 10^{-6}$ | $21.64 \times 10^{-6}$ |
| $CuO.Fe_2O_3$ | $6.93 \times 10^{-6}$ | $171.8 \times 10^{-6}$ * |

* Ferromagnetic.

(d) Structural examination of equimolar oxide mixtures.

An investigation of catalysis on mixed oxides would be assisted by information on structural properties of these oxides. Accordingly, an X-ray investigation was carried out on the $NiO/Mn_2O_3$ series and these findings are discussed below.

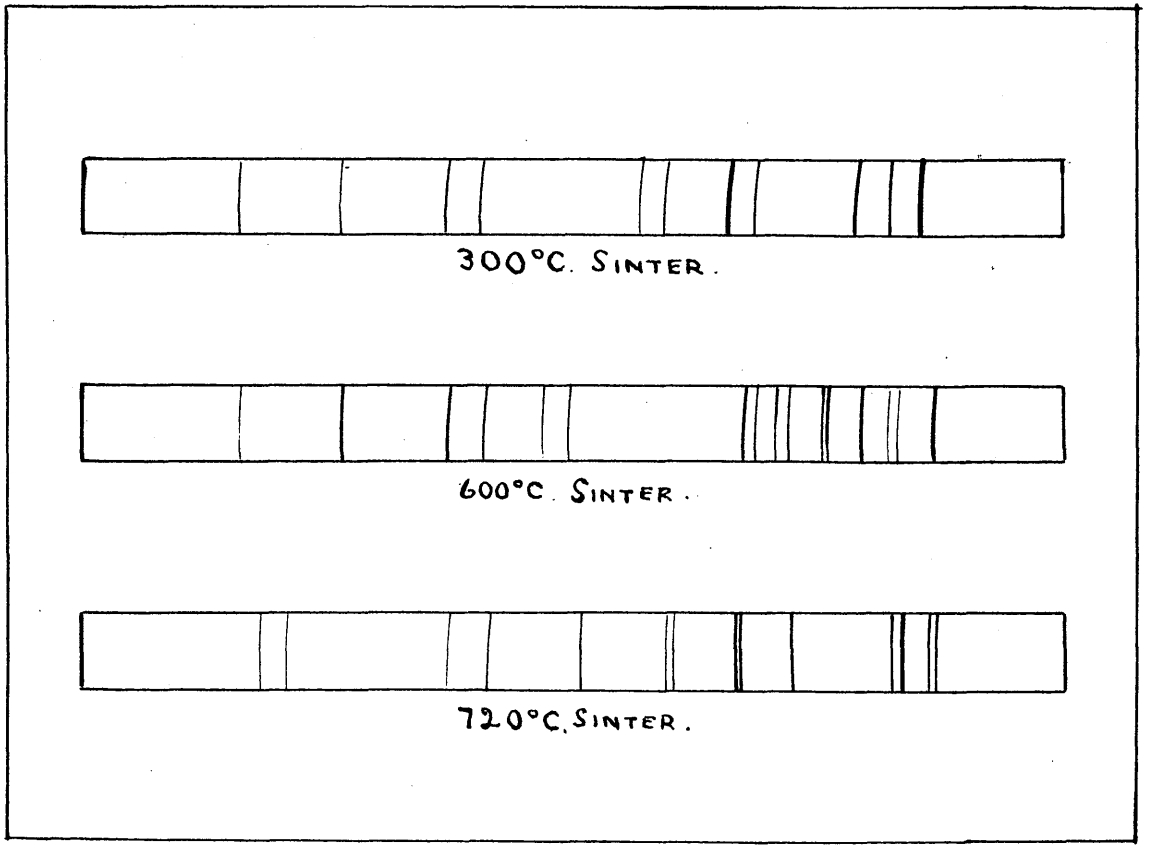
The trivalent oxides $Al_2O_3$; $Fe_2O_3$ and $Co_2O_3$ readily combine with CuO; ZnO and CdO to form oxides with a definite spinel lattice (113). This lattice has been described by Greenwald, Pickart and Grannis (114). It consists of a cubic close-packed system of oxygen atoms with divalent metal atoms situated in tetrahedral positions between the (110) planes, and trivalent atoms co-ordinated octahedrally to oxygen atoms, within the (110) plane between alternate rows of oxygen atoms. The term "inverted spinel" is used to distinguish a structure in which, in a unit cell, eight

of the divalent ions are switched to octahedral positions with eight trivalent ions in the tetrahedral interstices. In addition to these primary structures, partial inversions may occur giving rise to many possibilities for lattice distortion.

The only reference in the literature to a spinel structure of the type A. $Mn_2O_4$ was made over 50 years ago by Gorgeu (115). This author prepared a series of spinels, with A = Ni, Cu or Zn, by fusing the mixed sulphates and leaching out with acetic acid. The structure when examined by a microscope appeared to be of the cubic spinel type.

Since the spinel structure is generally associated with ferromagnetism (73), it was felt that the $NiO/Mn_2O_3$ sintered mixtures would be suitable for an X-ray investigation, as these mixtures alone of the $Mn_2O_3$ series exhibited ferromagnetism.

The X-ray data showed that with the preparations carried out below 600°C, the mixed oxide structure was inhomogeneous and consisted of three phases comprising the two single oxides and a solid solution of NiO in $Mn_2O_3$. At 760°C the structure had radically altered from that of the low temperature preparations as can be seen from Fig. C, where the series of powder photograph patterns are shown. It was felt that the high temperature preparation consisted of a solid solution of NiO in $Mn_3O_4$ or $Mn_2O_3$. No characteristic spinel lines could be detected. However the formation of the structure after calcination at 1000°C for some time has been demonstrated for other systems by Castell, Dilnot and Warrington (116) but was not pursued in this work as the intermediate mixtures are of more significant catalytic power as has been shown in the researches of Hüttig (73). (The author is indebted to Dr. P.J. Carter, Senior Lecturer,




PATTERN OF X-RAY POWDER PHOTOGRAPHS.
SHOWING STRUCTURAL CHANGES WITH SINTERING TEMPERATURE.
$NiO/Mn_2O_3$.

FIG.C

Metallurgy Department, Royal College of Science and Technology, Glasgow, for discussion on this point, and for advice on the interpretation of the X-ray photographs).

It can be seen from Table 28 that after sintering at 600°C the $CuO/Fe_2O_3$ mixture becomes ferromagnetic. According to Forestier (117) this is a true ferrite shown by X-ray examination to have the cubic spinel pattern. In this ferrite, $Cu^{2+}$ has approximately the same radius as $Fe^{2+}$ and there is a possibility of inversion of the position of the trivalent and divalent ions, so leaving a number of free valencies which will be effective in the catalysis. Unfortunately, time did not permit a more extensive study of this series, and considering the interesting trend of results a more detailed examination might produce some useful data.

(e) Relationship between liquid and gas phase catalysis.

As a comparison between the gas phase decomposition and that in the liquid phase, qualitative tests were made with the mixed oxide series $AO/Mn_2O_3$. These were carried out by adding 0.05 gm. of oxide (300 B.S. sieve) to 3 mls. unstabilised H.T.P. in a test tube. The mode of reaction was carefully observed, and the time of peroxide "disappearance" noted. The results are given in Table 31 below:-

TABLE 31. Liquid phase decomposition of 86% w/w $H_2O_2$ by $AO/Mn_2O_3$ mixed oxides.

| Catalyst | Temperature of preparation (°C) | Time of $H_2O_2$ "disappearance" | Remarks on mode of reaction. |
|---|---|---|---|
| $ZnO/Mn_2O_3$ | 300 | 38.8 secs. | Violent decomposition, |
| " | 400 | 35.8 " | Slow for 8 secs., then violent. |
| " | 500 | 3 mins | Initial inhibition (2½ mins) then very fast. |
| " | 600 | 34.6 secs. | Immediate fast reaction. |
| " | 760 | >48 hours | Very slow reaction. |

TABLE 31. Continued

| Catalyst | Temperature of preparation (°C) | Time of $H_2O_2$ "disappearance" | Remarks on mode of reaction |
|---|---|---|---|
| $NiO/Mn_2O_3$ | 300 | 47.0 secs. | Vigorous decomposition |
| " | 400 | 29.8 " | Extremely vigorous. |
| " | 600 | 30.0 " | Violent reaction. |
| " | 720 | >48 hours | Initial surge, steading to slow rate. |
| $PbO/Mn_2O_3$ | 300 | 21.7 secs. | Exceedingly violent |
| " | 400 | 23.0 " | " " |
| " | 500 | 25.0 " | Initially slow, (11secs), then extremely fast. |
| " | 600 | c.20.0 " | Explosive. |

The results show that the 300-600°C preparations are the best catalysts as in the vapour phase. Generally, the mixtures pre-treated at 600°C were the most effective, the $PbO/Mn_2O_3$ samples prepared at this temperature were violent in the catalysis. It may also be noted that the 720°C and 760°C sinters were relatively inactive as had previously been recognised in the gas phase work, but not to the same extent.

In general there seemed to be with most of the catalysts considered, an initial high efficiency, due perhaps to surface reaction. If this were so, then the surface heat produced would be very large and the catalysis would receive an initial impulse to carry it into an abiabatic zone. This would not necessarily be repeated at the next start, unless the special reactive property of the surface was restored on standing.

No example of such behaviour in the liquid phase work was found, although the pattern of behaviour has been easily demonstrated in the case of the vapour phase catalysis (Fig. 35).

(5) The influence of foreign ions in the catalysis by NiO.

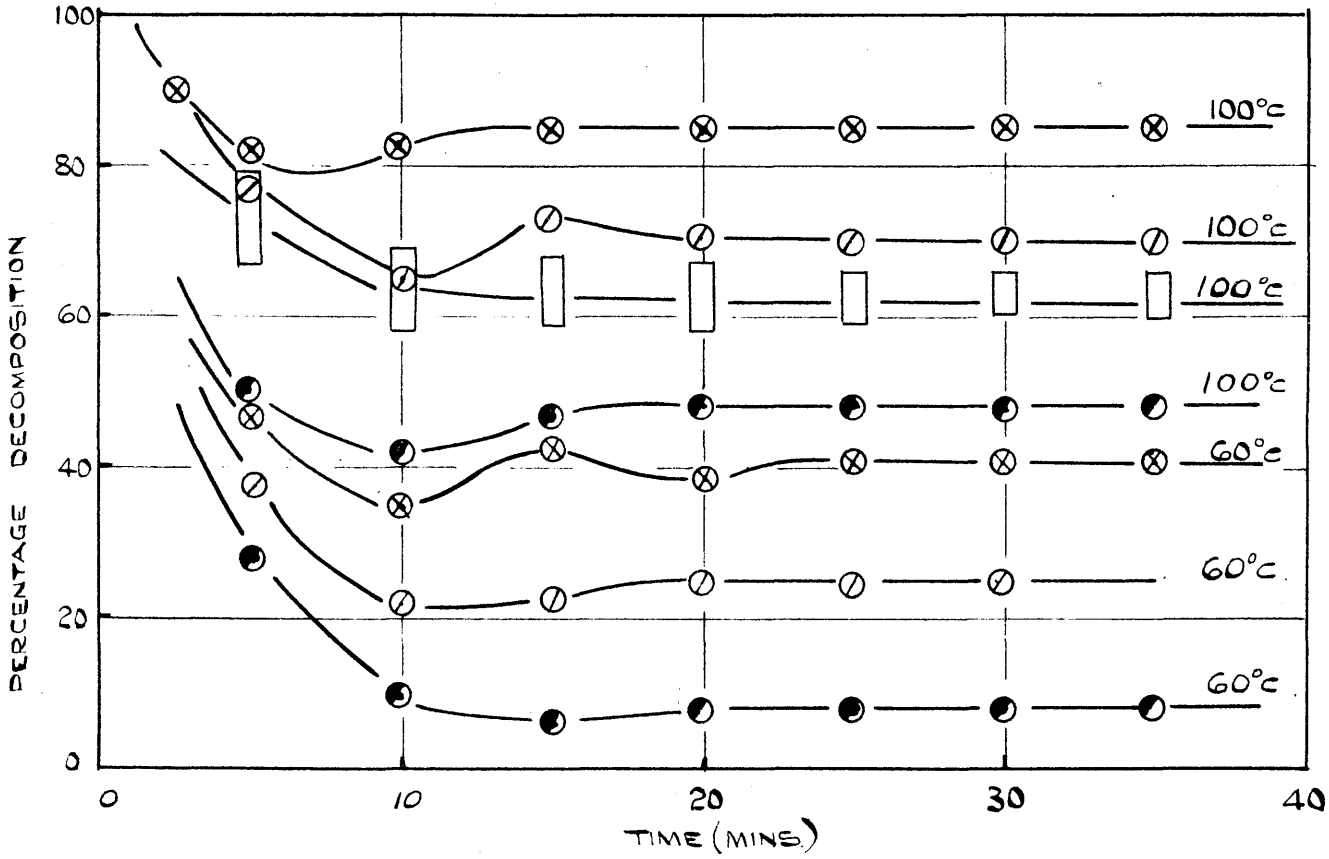
The catalytic properties of "green" and "black" nickel oxide slips have been reported in a previous paragraph. The work described in this section concerns an attempt to modify the catalytic properties of NiO by suitable additions of foreign ions which are well-known to modify the defect structure of the oxide.

Choice of foreign ion.

It is important in choosing the foreign ion that it should have a more or less fixed valency so that it shows no tendency to consume or part with electrons (118). It should also be about the same size as the ion in whose lattice it is to be substituted. Accordingly, $Li^{+}$, with an ionic radius of 0.60A°, and $Ga^{3+}$, ionic radius 0.62A°, were chosen as the ions most appropriating to these conditions for inclusion in the NiO lattice-in which $Ni^{2+}$ has an ionic radius = 0.69A°. The method of preparation of these oxides has been described under materials but it may be noted here that after firing, the $NiO/Ga_2O_3$ mixtures remained green in colour, while $Li_2O$ addition resulted in the formation of a black oxide.

Catalytic activity of "promoted" NiO.

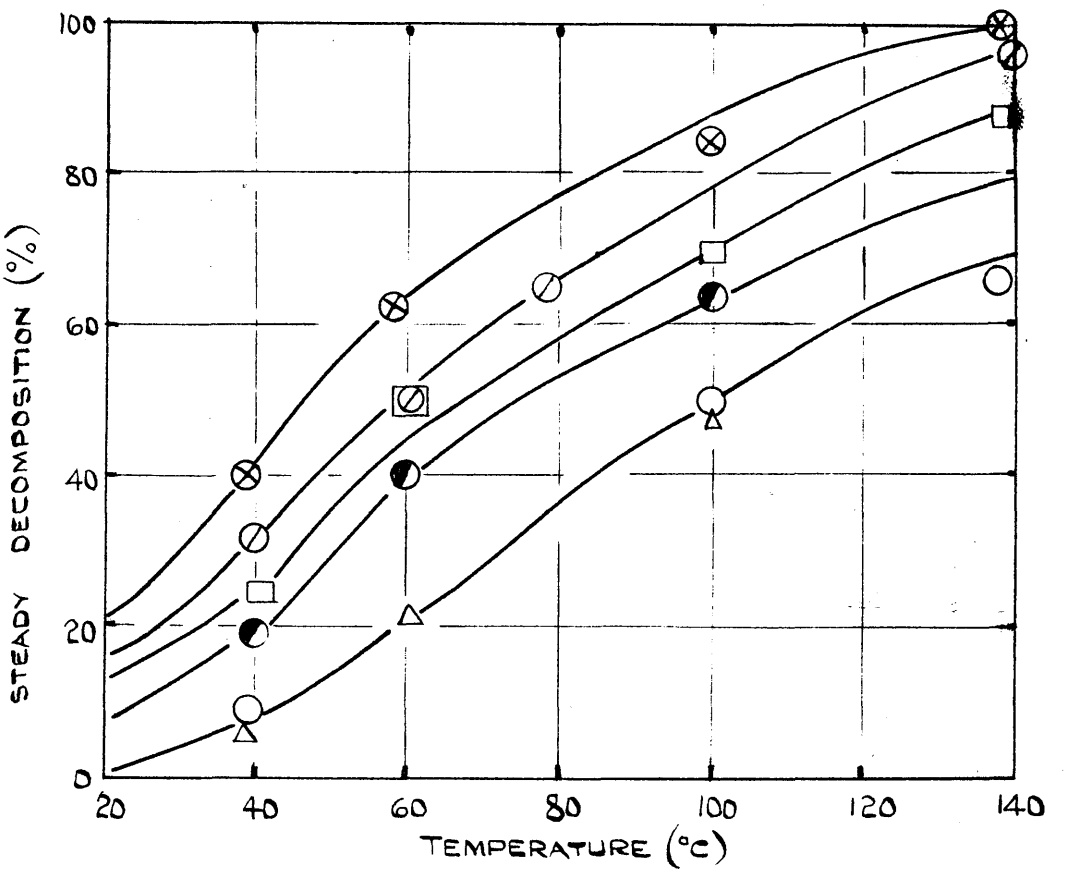
The NiO + x % $Li_2O$ series proved to be very effective in the catalysis. Unlike "black" nickel oxide, these oxides gave steady decompositions at a fixed temperature. There was no tendency, even on long (2-3 hours) exposure to $H_2O_2$ vapour, for the colour to change from black to green. The series containing $Ga_2O_3$ as the trace impurity were less active catalysts than those with $Li_2O$ inclusions, but at a given temperature gave more decomposition than stoichiometric NiO, pre-treated in the same way.




EFFICIENCY CHANGES ON FIRST EXPOSURE TO $H_2O_2$ (pp = 0·96 MM.Hg)

- ⊗ NiO + 11·5 MOL % $Li_2O$
- ◐ NiO + 0·024 MOL % $Li_2O$
- ⊘ NiO + 1·2 MOL % $Li_2O$
- ▯ NiO + 0·04 → 2·1 MOL % $GA_2O_3$ (ALL POINTS WITHIN INDICATED LIMITS)

FIG. 40




VARIATION IN ACTIVITY OF NICKEL OXIDE WITH DIFFERENT AMOUNTS OF $Li_2O$

○ STOICHIOMETRIC NiO
△ NiO + 0·024 MOL % $Li_2O$
◐ NiO + 0·24 MOL % $Li_2O$
□ NiO + 1·2 MOL % $Li_2O$
⊘ " + 2·4 " " "
⊗ " + 11·5 " " "

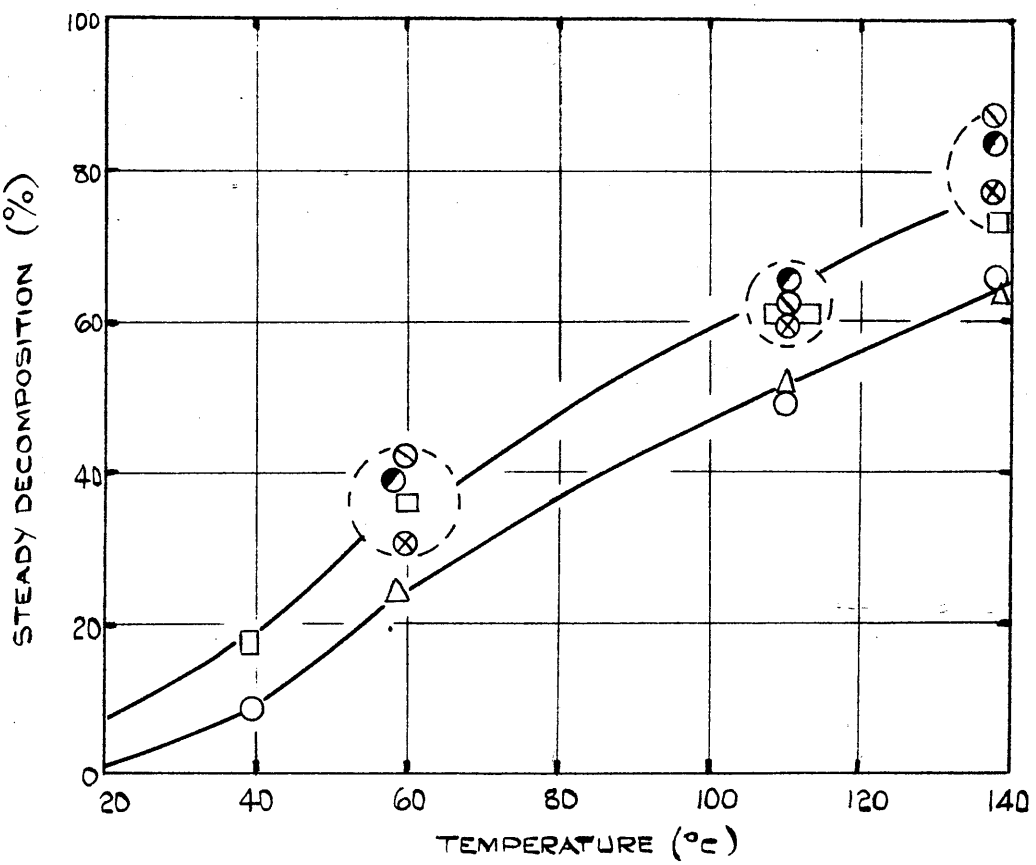
FIG. 41.

The initial efficiency variations on exposing the catalysts to $H_2O_2$ vapour followed a similar course on both series. Unlike the active single oxides, (PbO, NiO etc.) repetitive cyclic efficiency variations were not recorded, and in almost all instances the activity recovered to a steady value after an initial steady decline. This is illustrated for various runs in Fig. 40, which shows that in 20-25 minutes the rate had settled to a steady value.

Decomposition determinations were made at various temperatures in the region 38 - 138°C for all the catalysts in these series, and in Figs. 41 and 42 the steady decomposition values are plotted against the temperature at which they occur, for the $Li_2O$ and $Ga_2O_3$ series respectively. As the figures show, the nickel oxides containing 0.01% $Ga_2O_3$ and 0.01% $Li_2O$ by weight gave the same activity curve as that of the "green" NiO. The effect of adding $Li^+$ ions to the stoichiometric oxide was such as to markedly increase the catalytic activity as the $Li^+$ content increased. The effect of adding more than 0.004 mol% $Ga_2O_3$ was to increase the activity of NiO slightly at each temperature, and to remain at this value no matter how much $Ga_2O_3$ was added to the oxide. So that the curve joining up the activities of the $Ga_2O_3$ impurity series, has been taken at the mean position of all four points. It can be seen from Fig. 42, that deviations from this mean curve are very slight.

Temperature coefficient.

The temperature coefficient of the $Li^+$ impurity series was determined by making temperature changes from 100°C to 38°C to 60°C, and for the $Ga^{3+}$ series the changes were 100°C $\longrightarrow$ 60°C $\longrightarrow$ 136°C. Since the decomposition registered at 38°C with the latter series was usually negligible. The results of this investigation are given in tabular form below:-




VARIATION IN ACTIVITY OF NICKEL OXIDE WITH DIFFERENT AMOUNTS OF $Ga_2O_3$

○ — STOICHIOMETRIC NiO

△ — NiO + ·004 MOL. % $Ga_2O_3$

◐ — " + ·04 " " "

▭ — NiO + 0·2 MOL % $Ga_2O_3$

⊘ — " + 0·4 " " "

⊗ — " + 2·1 " " "

FIG. 42

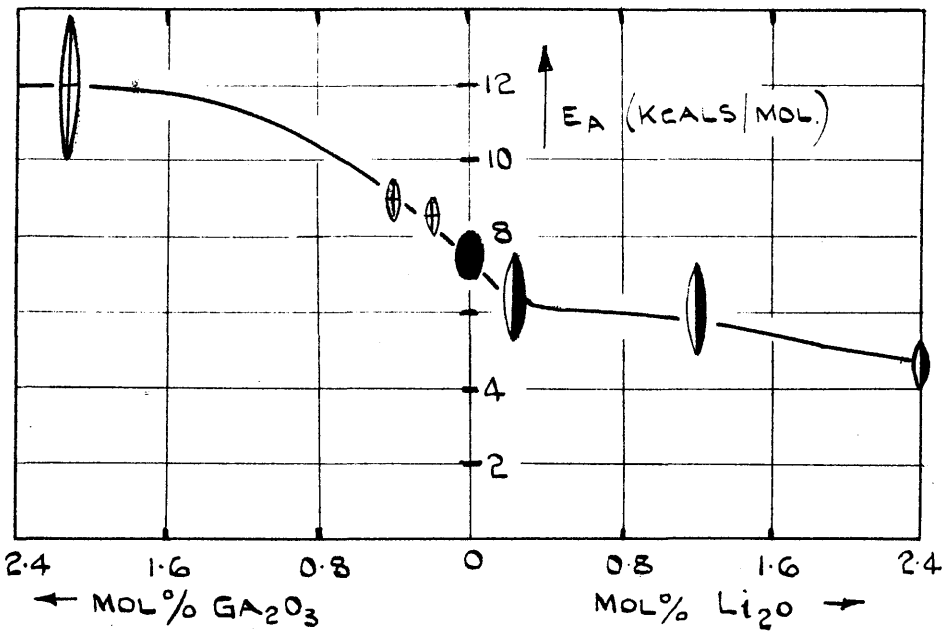
TABLE 32. Influence of $Li^+$ and $Ga^{3+}$ on the experimental activation energy of the reaction on NiO.

Rapid temperature changes.

| Oxide Composition | Percentage Decomposition | | | | Activation Energy (K.cals/mol.) | |
|---|---|---|---|---|---|---|
| | Steady 100°C | Initial 38°C | Steady 38°C | Initial 60°C | 100°C-38°C | 38°C-60°C |
| NiO "green" | 50.0 | 9.0 | - | - | 7.5 ± 0.5 | - |
| NiO+.024 mol % $Li_2O$ | 42.5 | 12.5 | 3.0 | 14.0 | 7.5 ± 1 | 15 ± 3 |
| " +.24 " % $Li_2O$ | 80.0 | 28.3 | 28.5 | 49.2 | 6.4 ± 1 | 8.0 ± 1 |
| " +1.2 " " | 70.0 | 26.1 | 25.2 | 45.0 | 6.1 ± 1 | 7.3 ± 1 |
| " +2.4 " " | 57.5 | 43.5(60°C) | - | - | 5.5 ± 1 | - |
| " +11.5 " " | 82.5 | 43.1 | 41.1 | 53.4 | 4.8 ± 0.5 | 6.0 ± 1 |

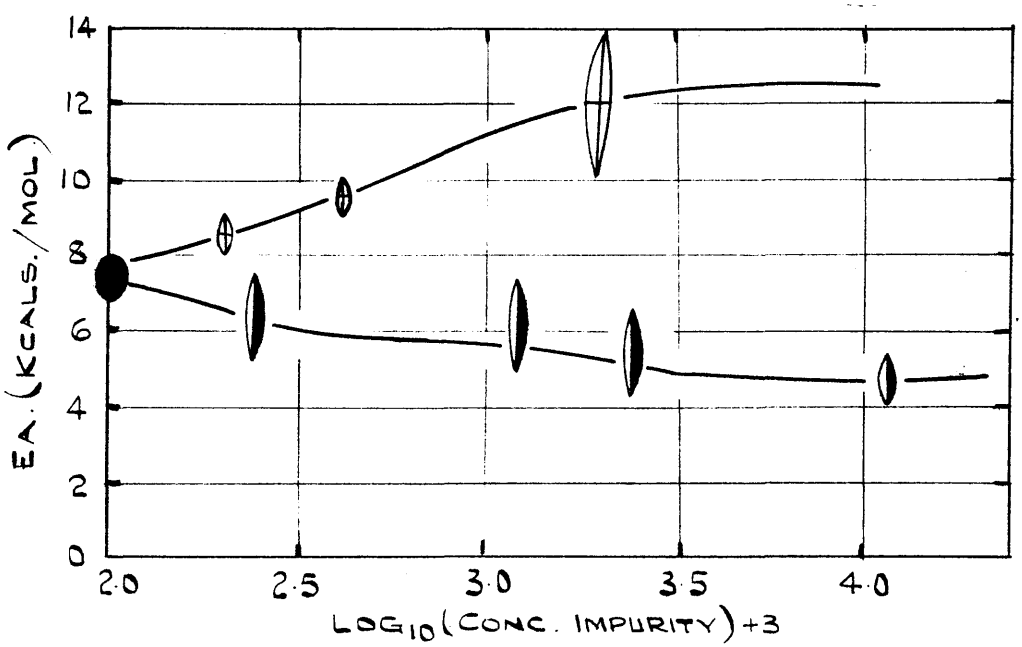
| Oxide Composition | Steady 100°C | Initial 58°C | Steady 58°C | Initial 136°C | Activation Energy (K.cals/mol.) 100°C-58°C | 58°C-136°C |
|---|---|---|---|---|---|---|
| NiO+.004 mol % $Ga_2O_3$ | 60.5 | 35.0 | 41.1 | 81.0 | 7.0 ± 0.5 | 5.7 ± 0.5 |
| " +.04 mol % $Ga_2O_3$ | 75.5 | 45.1(60°C) | 45.5 | 89.9 | 6.8 ± 0.5 | 6.0 ± 0.5 |
| " +0.2 " " | 61.5 | 25.1 | 36.7 | 78.5 | 8.5 ± 0.5 | 4.6 ± 1.0 |
| " +0.41 " " | 62.5 | 27.5 | 42.6 | 88.2 | 9.0 ± 0.5 | 5.6 ± 0.5 |
| " +2.1 " " | 60.5 | 17.5 | 30.0 | 82.0 | 12.0 ± 2.0 | 8.0 ± 2.0 |

The table shows that the effect of adding $Li_2O$ to NiO is to decrease slightly the activation energy of the reaction as the amount of $Li^+$ increases. This holds for an increasing and decreasing temperature change. On the other hand, $Ga^{3+}$ addition increases the activation energy in a decreasing temperature change, 100 - 58°C, but for an increasing change the value remains relatively constant. In comparing the two impurity effects the decreasing temperature




EFFECT OF IMPURITY ADDITION ON EXPERIMENTAL ACTIVATION ENERGY OF "GREEN" NICKEL OXIDE

FIG 43.




EFFECT OF IMPURITY ADDITION ON $E_A$ FOR 'GREEN' $Ni_0$ LOGARITHMIC PLOT

- "GREEN" $Ni_0$
- $GA_2O_3$ ADDITIONS
- $Li_2O$ ADDITIONS

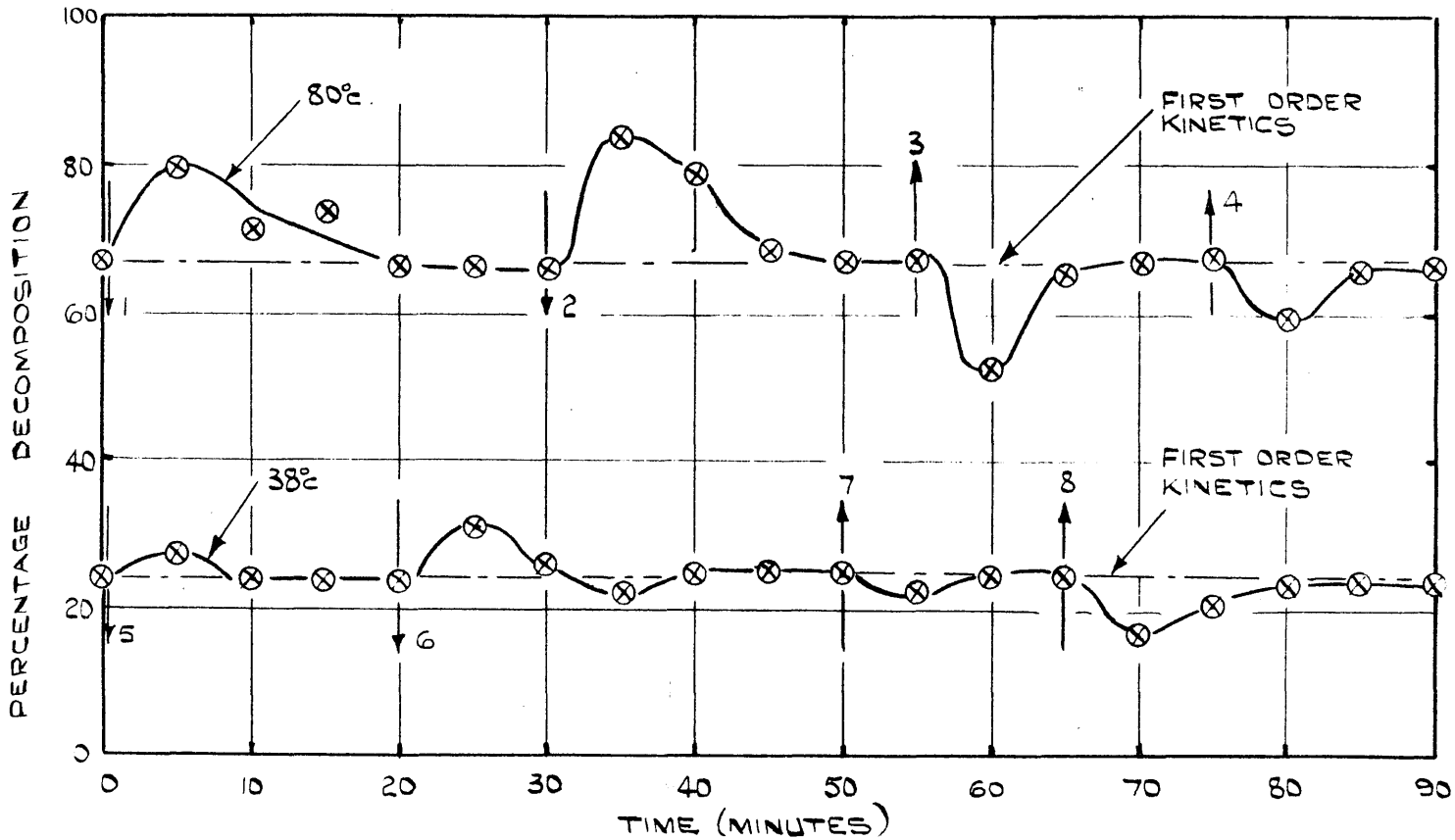
FIG.44.

changes are used since they refer in both cases to surfaces brought to a steady state at 100°C.

The effect of the $Li_2O$ and $Ga_2O_3$ trace additions on the experimental activation energy is shown in Fig. 43 in which the variation of the latter is plotted against the percentage impurity addition, and in Fig. 44 where $E_A$ is plotted against the logarithm of the impurity concentration. (It may be noted that the figures obtained for the decomposition in making the fast temperature changes cannot be strictly compared with the figures obtained in the efficiency determinations which apply to a fresh catalyst first exposed to $H_2O_2$ vapour at a constant temperature.)

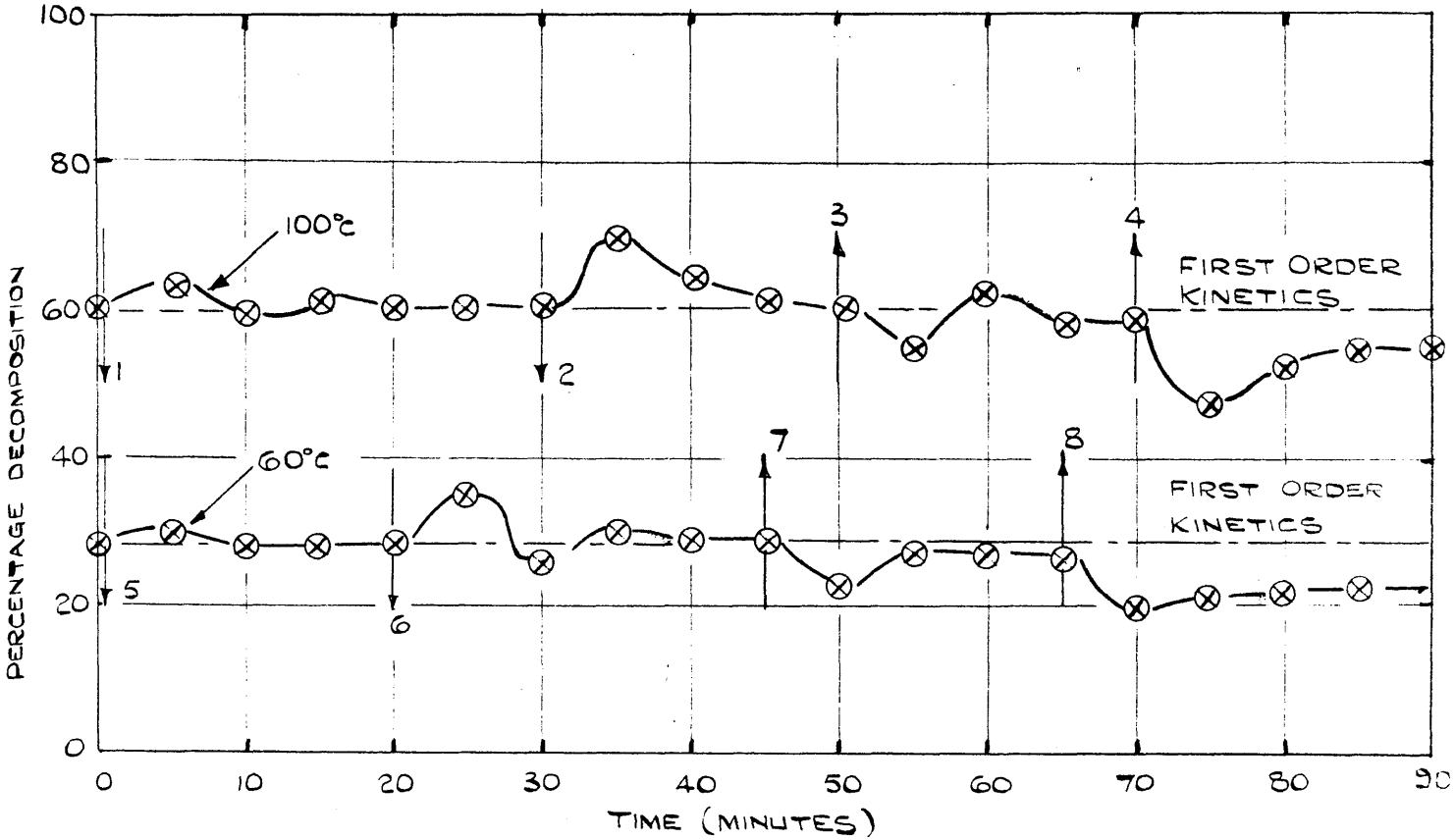
Reaction order.

The reaction order was studied on the NiO + 2.1 mol % $Ga_2O_3$ and 2.4 mol % $Li_2O$ mixtures with an initial $H_2O_2$ partial pressure of 0.96 mm Hg. The two catalysts behaved similarly on making fast concentration decreases, in that the same fraction of $H_2O$ vapour was decomposed at $C_i$, $2C_i/3$ and $C_i/3$, apart from a quickly damped cyclic variation on making the initial concentration changes. The reversal from $C_i/3 \longrightarrow 2\,C_i/3 \longrightarrow C_i$ was accompanied by an efficiency drop which was slightly more pronounced with $Ga^{3+}$ as the impurity and which was reminiscent of ZnO as a catalyst. This is illustrated in Figs. 45 and 46 for runs at different temperatures.




RAPID CONCENTRATION CHANGES $NiO + 2{\cdot}4$ MOL. % $Li_2O$.
PARTIAL PRESSURE $H_2O_2$ = 0·96 MM Hg ($c_i$)
POINTS 1, 5. $c_i \rightarrow 2c_i/3$
" 2, 6 $2c_i/3 \rightarrow c_i/3$
" 3, 7 $c_i/3 \rightarrow 2c_i/3$
" 4, 8 $2c_i/3 \rightarrow c_i$

FIG. 45




RADIO CONCENTRATION CHANGES $NiO + 2.1$ MOL% $GA_2O_3$.
PARTIAL PRESSURE $H_2O_2 = 0.96$ MM. Hg. ($c_i$)

POINTS 1,5. $c_i \rightarrow 2c_i/3$
" 2,6. $2c_i/3 \rightarrow c_i/3$
" 3,7. $c_i/3 \rightarrow 2c_i/3$
" 4,8. $2c_i/3 \rightarrow c_i$.

FIG. 46.

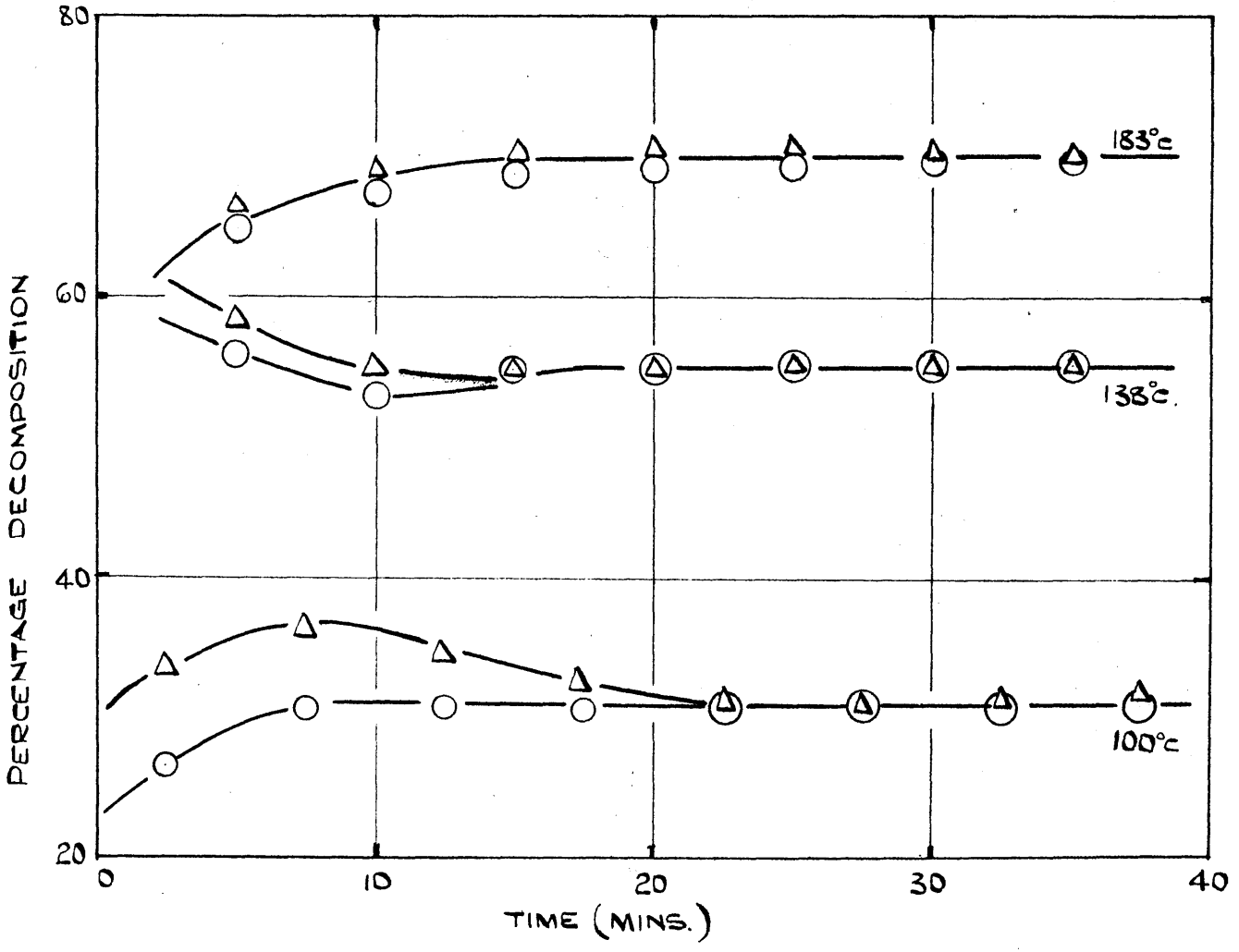
(6) The effect of highly paramagnetic ions on catalysis.

This was undertaken to see if the catalytic properties of an oxide could be influenced by the trace addition of a highly paramagnetic cation. For this purpose $Dy_2O_3$ was chosen, as it is one of the most paramagnetic oxides known; $Dy^{3+}$ having an effective magnetic moment of 10.5 Bohr magnetons.

A 5 mol.% addition of $Dy_2O_3$ was added to "green" NiO and the mixture heat treated at 600°C. This was contrasted with a 5 mol % addition of $La_2O_3$ to the same oxide; $La^{3+}$, effective moment zero. No difference in the catalytic behaviour of the two mixtures was detected, both were very active and gave steady decompositions of 40% at 38°C and nearly 70% at 76°C. The temperature coefficients were 4-5 K.cals/mol. However, these choices were perhaps unfortunate in that the trivalent lanthanon ions are 50% larger in diameter than $Ni^{2+}$ and would probably result in deformation, dislocation and ultimate collapse of the NiO lattice.

Accordingly, it was decided to extend this investigation to CdO, which was chosen because of its valency stability. The ionic radii ($Cd^{2+}$ = 0.97A°; $Dy^{3+}$ = 0.98A°) are almost identical.

The catalytic properties of CdO have already been described and it was shown to be a fairly poor catalyst. No improvement of activity of the catalyst was detected in adding 5 mol % $Dy_2O_3$ as a trace impurity as can be seen from Fig. 47, where the decomposition patterns of the two oxides are compared at 138°C, 100°C and 183°C.




EFFECT OF HIGHLY PARAMAGNETIC IONS ON CATALYSIS SHOWING ATTAINMENT OF STEADY EFFICIENCY LEVEL

○ CdO ; △ CdO + 5 MOL % $Dy_2O_3$.

FIG 47.

(7) The surface area measurements.

It may again be stated that the oxide slips were all compressed under the same pressure of 17.5 tons/sq. ins. and it would be expected that the surfaces would not vary much apart from micro pores which would contribute little to the catalysis.

When examined microscopically (x100), the slips presented smooth surfaces which did not vary from specimen to specimen. The same result was found when the surface areas were measured by a B.E.T. gas adsorption method ($C_2H_4$; -183°C). Eleven catalysts were measured and the roughness factors found to agree within a maximum range of 2 times. All of this roughness would not, however, be available for catalysis. It was concluded that the earlier assumption of the similarity of surface area was reasonable, and it was not considered necessary to extend the measurements to cover all the catalyst specimens examined.

From the Brunauer, Emmett and Teller (74) treatment of multilayer adsorption, we have:-

$$\frac{p}{v(po-p)} = \frac{1}{v_m c} + \frac{C-1}{v_m C} \cdot \frac{p}{po}$$

where v = volume at N.T.P. adsorbed at pressure p.

$v_m$ = " " " " when entire surface is covered by a unimolecular layer.

po = Saturated vapour pressure ($30.5 \times 10^{-3}$ mm. Hg. for $C_2H_4$ at -183°C).

C = exp. $(E_1 - E_L)RT$.

$E_1$ = Heat of adsorption of 1st layer.

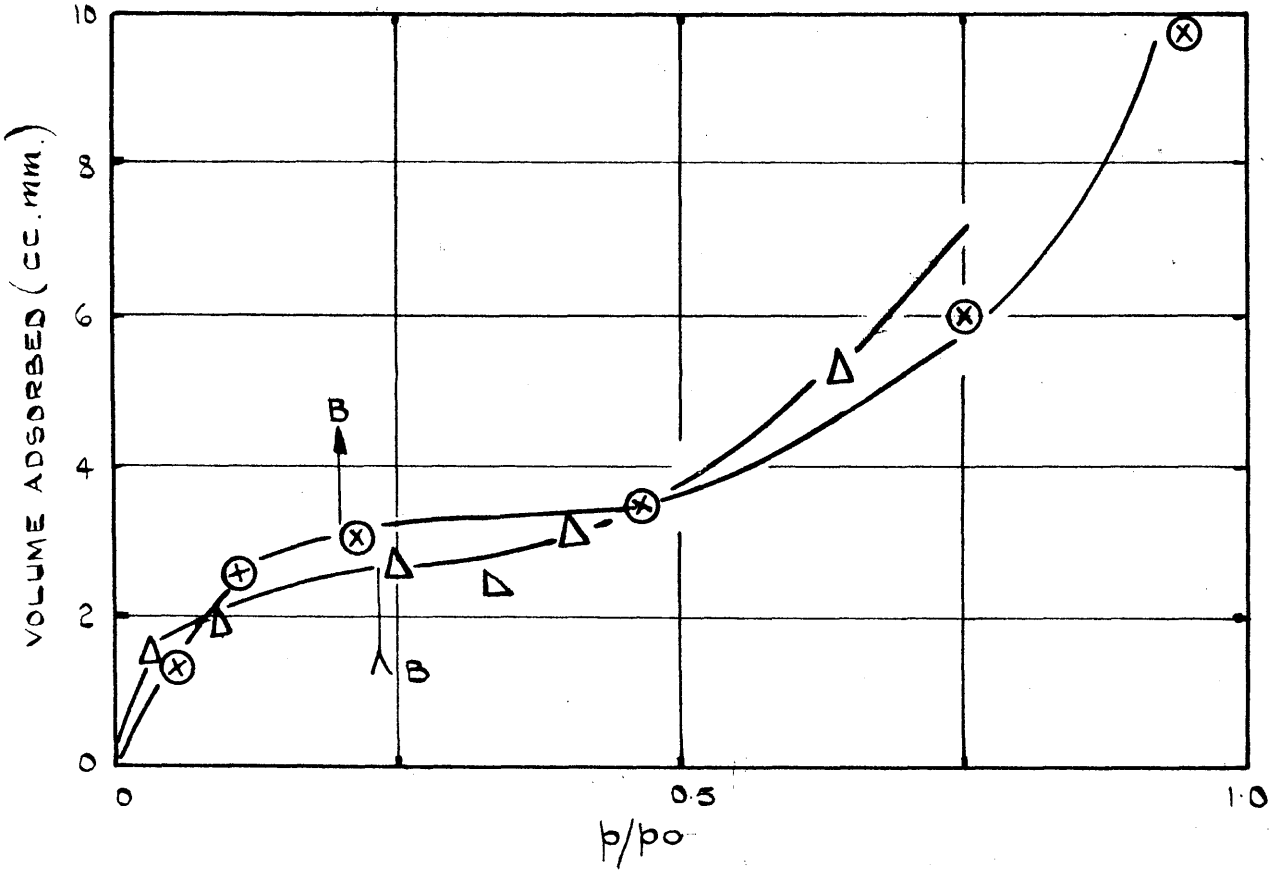
$E_L$ = Latent heat of vapourisation.

If the adsorption follows the B.E.T. treatment, then, a plot of p/v. (po-p) against p/po should give a straight line whose intercept is $1/v_m C$ and whose slope is $(C-1)\ v_m C$. Thus from the slope and intercept the two constants $v_m$ and C can be evaluated: the former being the volume of the monolayer. By plotting v against p/po, $v_m$ can also be determined from the point of inflexion on this curve.

Knowing the value of $v_m$ and using the conversion factor of 57.2 sq.cm/cc.mm. of adsorbed ethylene, as calculated by Wooten and Callaway-Brown (77) from X-ray data on the size of the $C_2H_4$ molecule, the surface area of the adsorbent is easily determined. The isotherms obtained are shown in Fig. 48 and were generally of Type 2 although one example of a Type 1 or Langmuirian isotherm was found with PbO, which result is probably not valid. The surface areas were all found by the "point B" method, since "B" was well defined, and the results are shown in Table 33 below.

TABLE 33. Surface areas of selected catalysts as determined by the "point B" method for $C_2H_4$/-183°C.

| Catalyst Composition | Sintering Temperature (°C) | Volume of Monolayer (cc.mm) | Surface area ($cm.^2$) | Roughness Factor * |
|---|---|---|---|---|
| PbO | 600 | 2.42 | 138.1 | 23 |
| $NiO/Mn_2O_3$ | 400 | 3.00 | 171.6 | 29 |
| MgO | 1000 | 1.98 | 113.2 | 19 |
| NiO+2.1 mol% $Ga_2O_3$ | 600 | 2.77 | 156.6 | 26 |
| NiO "green" | 600 | 3.23 | 184.3 | 31 |
| $Mn_2O_3$ | 600 | 2.10 | 120.0 | 20 |
| NiO+2.4 mol % $Li_2O$ | 600 | 2.79 | 165.8 | 28 |




SURFACE AREA ISOTHERMS ($C_2H_4$; −183°C)
SHOWING POINT "B"

⊗ $NiO/Mn_2O_3$ Δ $Al_2O_3$

FIG. 48

TABLE 33 (Continued)

| Catalyst Composition | Sintering Temperature ($^{o}C$) | Volume on Mono-layer (cc.mm) | Surface Area ($cm.^{2}$) | Roughness Factor * |
|---|---|---|---|---|
| $PbO/Mn_2O_3$ | 400 | 2.32 | 132.2 | 22 |
| ZnO | 600 | 2.11 | 120.5 | 20 |
| $CuO.Fe_2O_3$ | 600 | 2.01 | 110.9 | 18 |
| $Al_2O_3$ | 1000 | 2.89 | 165.0 | 27 |

* Roughness factor to nearest whole number.

It is evident from the above table that the roughness factors are in the region 18-31, while most lie between 20 and 30 i.e. a factor of 1/2 in the surface area. No attempt was made to follow change of surface area with sintering because of the procedure adopted in preparing the catalyst slips.

(8) Static system results.

A few blank experiments were carried out with the empty vessel and no decomposition was observed at temperatures up to 180°C.

This inactivity of the glass surface was in marked contrast to the results of Giguère (34), and was confirmed carefully with all the pyrex reaction chambers used.

A brief investigation was carried out with "black" and "green" NiO in the temperature range 21 - 211°C. The results with the stoichiometric oxide were easily reproducible but "black" NiO showed appreciable deactivation after being in contact with the peroxide vapour. With "green" NiO no decompositions were observed in this system until temperatures greater than 100°C whilst "black" NiO was active at temperatures c.30°C. The following table shows the results obtained when a fresh catalyst was exposed to $H_2O_2$ vapour at 43°C.

TABLE 34. Decomposition of $H_2O_2$ vapour on "black" nickel oxide at 43°C. Static system.

| Time (minutes) | Total Pressure (mm. di-butylphthalate) | Partial pressure $H_2O_2$ (mm. di-butylphthalate.) |
|---|---|---|
| 0 | 16.75 | 16.5 |
| 1 | 17.75 | 14.5 |
| 2 | 18.50 | 13.0 |
| 3 | 19.00 | 12.0 |
| 4 | 19.50 | 10.5 |
| 5 | 20.00 | 9.5 |
| 6 | 20.50 | 8.5 |
| 7 | 20.50 | 8.5 |

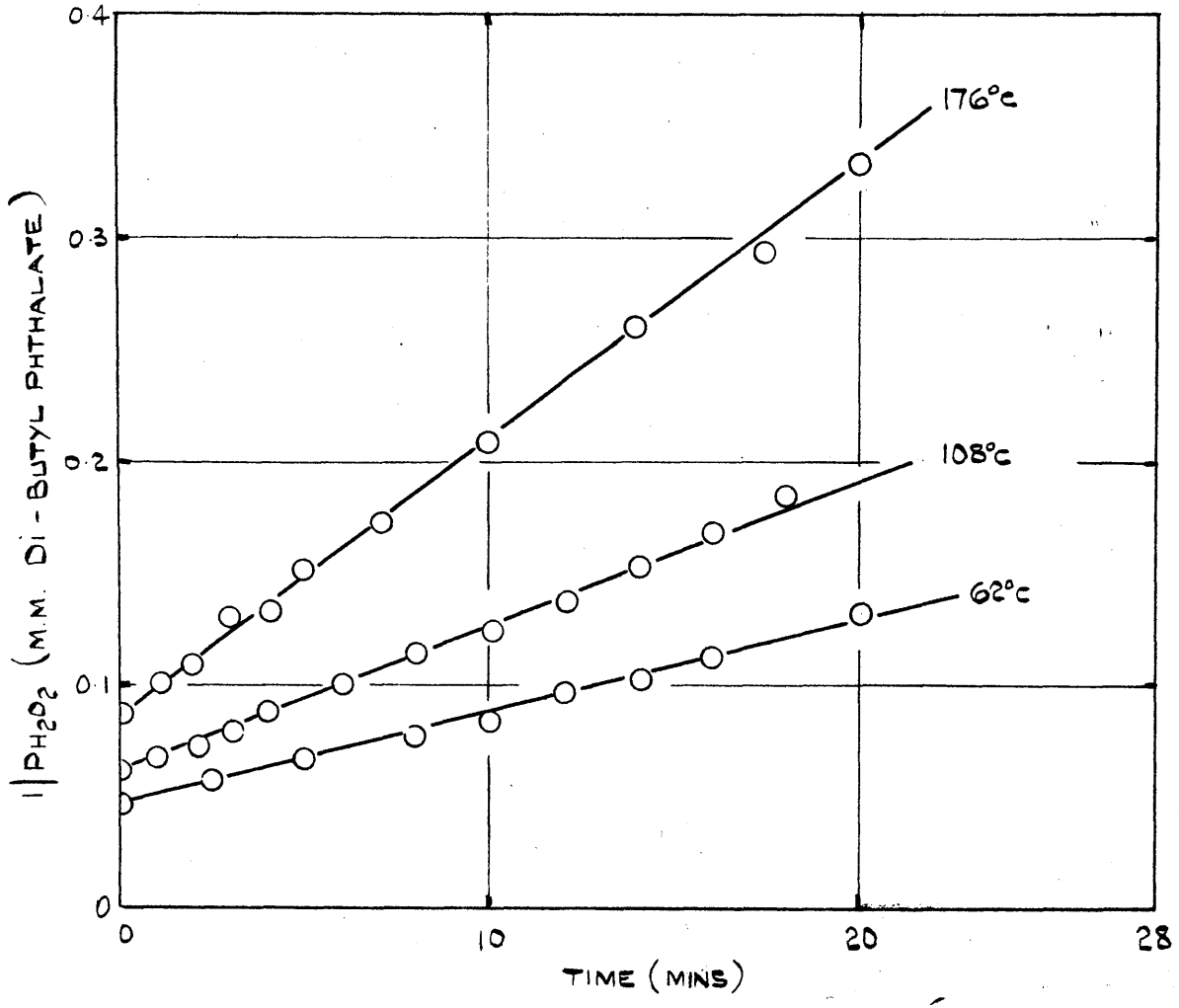
TABLE 34. (Continued)

| Time (minuted) | Total pressure (mm. di-butylphthalate) | Partial pressure $H_2O_2$ (mm. di-butylphthalate.) |
|---|---|---|
| 8 | 21.00 | 7.5 |
| 10 | 21.50 | 6.5 |
| 12 | 22.00 | 5.5 |
| 15 | 22.50 | 4.5 |
| 20 | 23.50 | 2.5 |
| 25 | 24.00 | 1.5 |
| 30 | 24.50 | 0.5 |
| 35 | 25.00 | 0.0 |

Determination of reaction order.

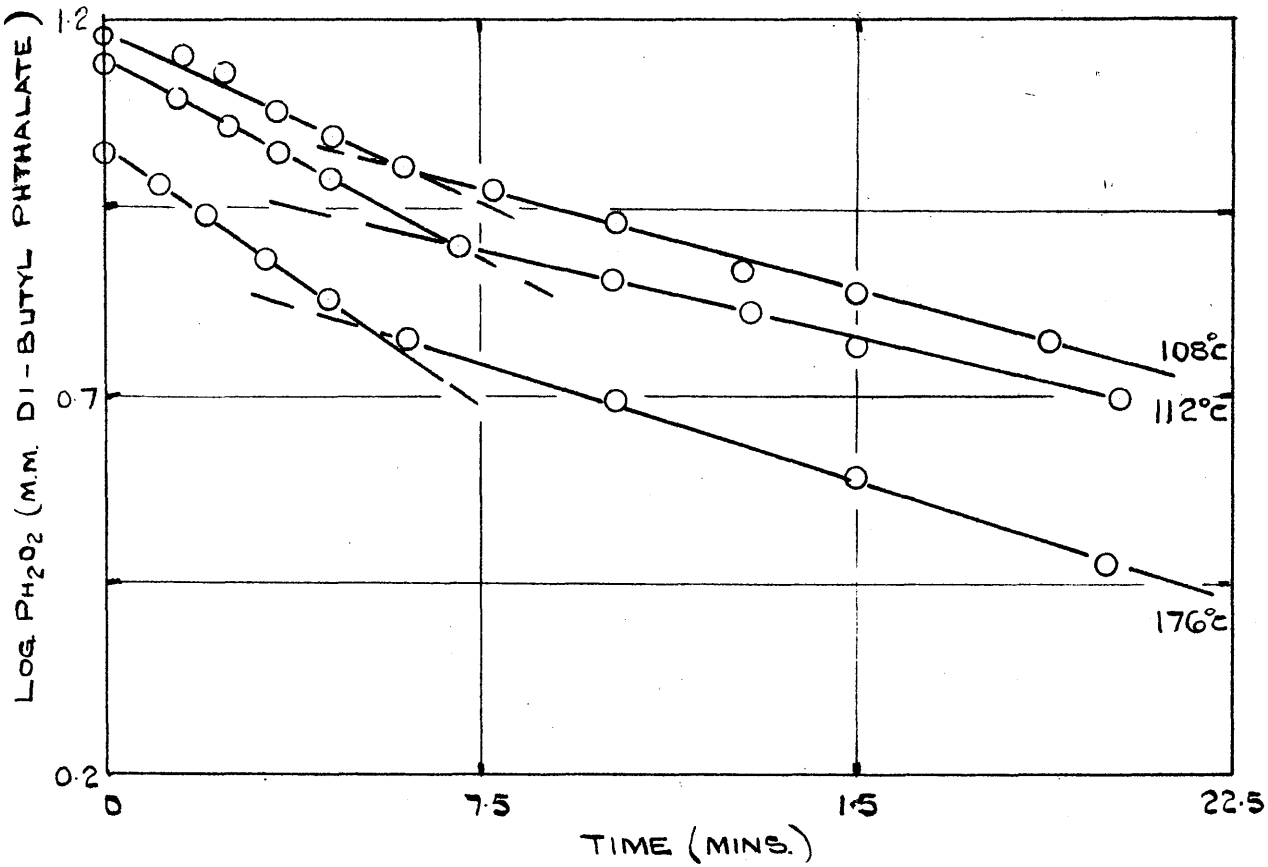
These experiments were made with an "equilibrium oxide", which was reached after several hours exposure of "black" NiO to peroxide vapour. A difficulty here is that the efficiency of the so called "equilibrium oxide" is dependant on the concentration of $H_2O_2$ vapour and could vary in the course of a run. This uncertainty cannot be avoided in a static system.

The determination of the order is shown in Figs. 49 & 50 where first and second order plots are made. At first sight there would appear to be complete support for second order. This was similar to that found by Mackenzie and Ritchie (32) for the decomposition on quartz with similar partial pressures of $H_2O_2$. However, for a fall in $C_{H_2O_2}$ to 50% of the initial value a very satisfactory agreement with the first order law was obtained, which accords with the flow results.




DECOMPOSITION KINETICS. "EQUILIBRIUM"
NICKEL OXIDE. SECOND ORDER PLOT

FIG. 49




DECOMPOSITION KINETICS, "EQUILIBRIUM" NICKEL OXIDE.
FIRST ORDER PLOT SHOWING TRANSITION TO SLOWER RATE

FIG. 50

It is felt that these results must be explained by assuming that slowness of mixing caused the fall off in the rate of decomposition which appears to suggest second order, which may also explain the results of Mackenzie and Ritchie (32); of course, gentle fall off in the catalyst efficiency may also be a factor in this apparent transition.

Temperature coefficient.

The temperature coefficient of the first order rate constant for the reactions at 176°C and 108°C leads to an $E_A$ value of 4.6K. cals/mol. This is a slightly lower value than that found in the flow system (6.5 K.cals/mol) for a similar oxide and probably results from similar reasons as those outlined above.

DISCUSSION

In this section the experimental results will be examined and discussed in detail.

The first section is concerned with the method employed in this investigation, following which the various factors which may be connected to form a basis for comparison of catalytic activity will be discussed. Other general sections deal with the reaction mechanism, the Arrhenius parameters - leading to the discussion of the Compensation Effect; and the interpretation of the other physical data e.g. magnetic susceptibility and surface areas. Detailed discussion is given separately of nickel oxide and spinel-type systems as catalysts.

(1) The method of investigation.

Flow systems as methods of investigating heterogeneous catalytic reactions in the gas phase have been widely used. Precise studies such as those of Schwab and Pietsch (120) and Palmer and Constable (121) who both used a catalyst concentrated at one point in a flowing gas established the method. A more elaborate example of its use was Twigg's (122) very detailed study of the oxidation of ethylene on Ag by using the catalyst in the form of short lengths of wire. Recent examples of fundamental studies based on flow systems include Hauffe, Glang and Engell (51) in an investigation of the $N_2O$ decomposition on various catalysts based on nickel oxide. Parravano (53) and Kul'kova and Temkin (123) on the $CO/O_2$ oxidation on NiO and the water gas reaction on $Fe_2O_3$, and, very recently Darby and Kemball (124) on the methanol decomposition on a Fischer- Tropsch catalyst.

The advantages of the flow over the static method are numerous. By working with one flow rate throughout, all the catalysts were examined under

the same flow conditions at a given temperature. Catalysts could also be studied with steady $H_2O_2$ concentration for any length of time necessary, so that slow changes in the efficiency of the catalyst, itself, could be followed. This is, of course, impossible in a static study in which the $H_2O_2$ concentration, and hence the working rate of the catalyst, varies during a run. As stated previously the validity of static studies depends entirely on the assumption that any changes in the catalyst are either so fast as to follow, without appreciable lag, the steady fall in substrate concentration, or, that they are so slow as to leave the catalyst unchanged in the course of a convenient experiment.

As shown in the results and experimental sections, the flow method gave excellent reproducibility of results with oxide and metal/metal oxide catalysts which had been closely controlled in their preparation. This, latter point must be emphasised since a catalyst's activity is dependant on its "previous history" and reproducibility depends on the care taken to match the pre-treatment of each sample. Reproducibility obtained in the brief static investigation was not of a high order even after allowing a catalyst an original settling down period to "condition" the surface to $H_2O_2$.

Practical advantages for these experiments have been referred to already. The need to limit temperature rise at a catalyst on which there is a measureable amount of decomposition requires that a diluent gas be used. This could introduce difficulties with gas phase diffusion, which are readily avoided in a flow system.

(2) The activity of single oxides in the catalysis of $H_2O_2$.

The results have shown that the efficiencies of the catalysts examined vary over a wide range, and it is hoped now to draw attention to relationships between known properties, chemical and physical, and catalytic efficiency. In simple words we seek to answer the question - "What makes a substance a good catalyst ?"

But first it must be decided what quantitative criterion is to be used to designate the efficiency of a given catalyst. Consider the comparison between MgO - no decomposition in the present apparatus at 100°C, and PbO which gave 100% decomposition at this temperature, and therefore neither can be over-lapping. The first need here then is clearly for a satisfactory relationship between temperature and efficiency for each catalyst.

In the past, many methods have been used for distinguishing different catalysts in the same reaction in order to provide a basis of comparison. The choice of this criterion is not, by any means, a simple matter to decide, since, it is doubtful if any single measurement will provide all the data required to formulate an adequate activity series. Hauffe, Glang and Engell (51) in a study of the $N_2O$ decomposition on metal oxides compared the catalytic activities by the amount of decomposition each specimen gave at various temperatures. In a somewhat analogous manner Beeck (125) used the rate constant, which in the present work may be substituted for % decomposition, as a criterion of catalyst activity for the $C_2H_4$ hydrogenation on Cu, Au and Ag catalysts. Dell, Stone and Tiley (45) have also formulated a series for the $N_2O$ decomposition in which the efficiency of the catalyst is considered to be indicated by "the temperature required to produce measurable decomposition", which is a more useful method in the $N_2O$ than $H_2O_2$ decomposition because of the wider temperature range

(250-700°C) found in the former for the various surfaces.

In addition to the above, very many investigators have used the values of the activation energies in a heterogeneous surface reaction to indicate catalyst activity. For example, Kemball (126) in investigating the ammonia/deuterium exchange on Pt, Rh, Pd, etc., and Couper and Eley (127) have used the energy of activation for the ortho-para hydrogen conversion to compare the efficiencies of Pd/Au alloy catalysts, which they later contrasted with the magnetic susceptibility of these samples.

In the present experiments the catalysis was studied on all the oxides at different temperatures and the steady decomposition found, after the initial fluctuations had settled. In addition, by making rapid temperature changes, experimental activation energies were obtained which were considered to be related to the $E_A$ appropriate to a particular configuration of the surface from which the temperature change was made. Thus, if temperature changes were made either up or down at temperatures $T_1$, $T_2$ and $T_3$ °K then three slightly different $E_A$ values were found for each temperature which was held to be indicative of the changing nature of the catalyst surface at $T_1$, $T_2$ and $T_3$ °K respectively. This is discussed more fully later.

A comparison of D values implies identical total surface areas, and special heat or other pre-treatment might, and probably will, affect different oxides quite variously. This has been shown in the case of $Ag/Ag_2O$ where the etched catalysts gave a higher decomposition at the same temperature than the "normal" catalysts. Also, activation in hydrogen of $Al/Al_2O_3$ resulted in a catalyst which at 183°C gave 85% decomposition~~ing~~ whereas the normal specimen gave less than 2%.

However, the $E_A$ factor should be independant of the total surface area

present, although it too is dependant on pre-treatment but less so than D. Here, it must be stated that the variations in D with temperature of pre-treatment in the $Mn_2O_3$/AO series cannot be related to a difference of area since these catalysts were all sintered before pressing into slips.

It is assumed, as will be discussed later, that at all the catalysts in this range there are a number of possible reaction paths common to them all. Each path is associated with an $E_A$ whose value is adjustable between certain limits, decided by the type and proportion of the reaction paths and is, in fact, fixed by the solid catalyst - by its chemistry and by its method of preparation and heat treatment. The overall process at one catalyst will exhibit an $E_A$ which is characteristic of the surface, but when comparing two surfaces it is necessary to bear in mind that we are not necessarily dealing with identical surface reaction paths. This will apply even to catalysts of the same chemical constitution although with much greater force to different types of catalysts such as $Al_2O_3$ and PbO.

Thus, relevant to each temperature, for each catalyst we have two measured values D and $E_A$, which refer to a given state of each catalyst. Now, within each of the three oxide groups studied, it is fairly simple to compare the efficiency of each member by the amount of decomposition each gave at a certain temperature. For instance, we may compare $Mn_2O_3$, PbO, $Ag_2O$ etc. through the decomposition each gave at, say 38°C. Similarly $Fe_2O_3$, CuO and CdO may be compared by their efficiencies at 140°C.

Alternatively, a comparison of activity could be made by considering the temperature at which each oxide gave a definite, say 50%, decomposition. This value if not obtained experimentally may be derived by interpolation or

extrapolation from the activation energy data which, however, implies that the nature of the catalyst surface is unchanged at the derived temperature, and would therefore give a different T value than that yielding a steady decomposition of 50%.

A strict comparison of experimental activation energies is complicated through the intervention of variable heats of adsorption factors which will alter with the oxide surface and the temperature of this surface. In any case, if different reaction mechanisms were involved for the various oxides then the experimental $E_A$'s could not justifiably be compared. This would be a major obstacle in the analysis of the rate data and would not strictly allow the oxides to be compared beyond their separate groups, always assuming that in each group the catalysis mechanism would be the same for every member.

Bearing the above provisos in mind, it was decided that for the present reaction the best method of comparing the catalyst activities would be to use the steady decompositions found at a certain temperature and, but with less emphasis on, the apparent energy of activation at this temperature.

Now, considering the catalysis results obtained with the metal/metal oxides of class (1) i.e. the catalysts active at room temperature to 100°C. At 100°C, Co/CoO gave 100% decomposition. The oxides of Cu, Mn and Ag gave decompositions from 80-90%, whilst Ni/NiO (including it in this group) gave 11.5%. The apparent energies of activation in this region are 4-5 K.cals/mol for Mn/MnO and $Ag/Ag_2O$, and 12-16 K.cals/mol for Co/CoO, $Cu/Cu_2O$ and Ni/NiO, with the $E_A$ values of the specimens increasing in the order written. In this instances, the $E_A$ figures provide the main basis for the following series as the D values at 100°C were in very close proximity:-

$$Mn/MnO \geq Ag/Ag_2O \geq Co/CoO > Cu/Cu_2O \gg$$

$$Ni/NiO.$$

Similarly for class (2), Zn/ZnO at 138°C gave a percentage decomposition after 40 minutes of 28% (falling), and an $E_A$ = 33-34 K.cals/mol whilst for $Fe/FeO/Fe_2O_3$ these values are 78% and 20 K.cals/mol respectively. Then, in class (3) $Al/Al_2O_3$ at 183°C gave $\leq$ 2% decomposition, and $Sn/SnO_2$ 65-70% after 90 minutes, a falling value, and an $E_A$ = 26 - 27 K.cals/mol. The $E_A$ for $Al/Al_2O_3$ was not determined because of lack of activity in the temperature range studied, but in the special case of the activated $Al/Al_2O_3$ slip at 183°C decompositions of $>$ 90% were found and an apparent energy of activation of 18-19 K.cals/mol.

So that, combining the data found with all the metal/metal oxides to give an activity series, we have:-

$$Mn/MnO \geq Ag/Ag_2O \geq Co/CoO > Cu/Cu_2O \gg$$

$$Ni/NiO \geq Fe/FeO/Fe_2O_3 > Al/Al_2O_3 \text{ (activated)} >$$

$$Zn/ZnO = Sn/SnO_2 > Al/Al_2O_3 > \text{glass}$$

On the same basis, for the catalysis occurring on the pure bulk oxides the following activity series may be formulated:-

$$Mn_2O_3 > PbO > CoO/Co_2O_3 > NiO \text{ "green"} >$$

$$CuO > Fe_2O_3 > CdO > ZnO = MgO >$$

$$\alpha\text{-}Al_2O_3 > \text{glass (pyrex)}.$$

In the above series the first four oxides gave decompositions of 85%, 55%

and 10% at 38°C respectively, and had activation energies at a temperature drop to this temperature of 5.9 - 8 K. cals/mol. The next three oxides did not give 40% decomposition until above 100°C, apart from CuO, but at 100°C the decompositions were CdO (32%), $Fe_2O_3$ (38%) and CuO (50%). The activation energies for rising and falling temperatures were 11, 22 and 15 K.cals/mol for CdO, $Fe_2O_3$ and CuO respectively.

ZnO, MgO and $\alpha$ - $Al_2O_3$ were ineffective catalysts, the latter two being subjected to heat treatment at 1000°C before they registered any appreciable decomposition, which at 183°C was between 35 and 40%. The experimental EA's were greater than 25 K.cals/mol and could not be determined accurately because of the inactivation incurred during contact with $H_2O_2$ vapour.

Having formulated the catalysts into these series of descending activity, we must now consider if there exists a physical or chemical basis by which we may endeavour to explain this difference in properties. That is, we must now consider answering the question posed in the first paragraph of this section.

Considering first the basicity of the oxides, it can be seen that they are all basic, but if this alone was an accurate criterion then it would be expected that the trivalent amphoteric oxides $Al_2O_3$ and $Co_2O_3$ etc. would occupy similar positions. This is not the case, since there is a very wide difference in activity between $Mn_2O_3$, $CoO/Co_2O_3$ and $\alpha$ -$Al_2O_3$. So that the proton attracting properties of these surfaces are apparently not of much significance in determining the order of this series.

As to the stability of the oxides, the ease of reduction by hydrogen of the oxides of Fe, Co, Ni and Cu decreases in that order, which, apart from the position of iron is somewhat analogous to the decreasing efficiency of the catalysts given above. At the high efficiency end of the list is placed

$Ag/Ag_2O$, which begins to decompose at 240°C, and at 300°C is completely stripped of oxygen. On the other hand, alumina, an inactive catalyst, is an extremely stable oxide with a very high heat of oxidation similar to $SnO_2$. However, PbO is just as stable as CdO or CuO and is 3-4 times more active in the catalysis. So that, although there exists these relationships between activity and oxide stability, certain anomalies are obvious which cannot be explained on this basis alone.

Re-examining the two series, it can be seen that from PbO to NiO there exists a common factor in the electronic structure, in that they are normally all p-type semi-conductors in which the stoichiometic oxide tends to adsorb oxygen. In the rest of these series from CuO to $SnO_2$ we have only n-type and insulator oxides. Apart from ZnO, the n-type oxides were better catalysts than the insulators. ZnO and Zn/ZnO were inactive catalysts with an apparent $E_A$ of 33.8 K.cals/mol only becoming appreciably active at 138°C, and in essence there was little difference in activity between them and MgO. Otherwise, the series assume regular patterns in that, following the p-type oxides we have a group of n-type, or oxygen losing semi-conductors in which the metal is usually present in excess of stoichiometry; and then the insulators MgO, $Al_2O_3$ and $SnO_2$, which are normally non-conductive at ordinary temperatures.

The fact that oxide activity in the catalytic decomposition of $H_2O_2$ vapour may be successfully related to the semi-conducting properties of the oxide leads to a comparison of the above data with that given by Dell, Stone and Tiley (45) for the $N_2O$ decomposition and by Stone (56) for the $CO/O_2$ reaction. For the former reaction the authors show that the oxide activity falls in the sequence p-type > insulators > n-type, whilst for the $CO/O_2$ oxidation, Stone has shown the series to be p-type > n-type>insulators.

So that, without discussing this comparison further in the meantime, it would appear from these activity series that the present reaction is related more closely to the $CO/O_2$ oxidation than to the $N_2O$ decomposition, as far as the oxide activities are concerned.

Further to these pointers, it has been shown that $Al/Al_2O_3$, when used as the normal oxide covered metal, is inactive in the reaction giving about 2% decomposition at 183°C, but when this same oxide was subjected to treatment with hydrogen at 600°C for several hours, it became active giving 40 times the decomposition at the same partial pressure of $H_2O_2$. The $Al/Al_2O_3$ was thus activated by this procedure, which owing to the stability of $Al_2O_3$ would certainly not strip the oxide from the surface. It seems probable that some oxygen may be removed, leaving a surface with a metal excess or n-type character. The metal/metal oxide was then found to be similar in activity to $Fe/FeO/Fe_2O_3$. So that this treatment may be considered to have increased the electronic conductivity of the surface by producing aluminium atoms which dissociate into aluminium ions and an equal number of quasi-free electrons which may then initiate the reaction.

Similarly, heating MgO and $\alpha$-$Al_2O_3$ to 1000°C for some time, may give rise to anionic vacancies (116), and when the oxides are quickly cooled to room temperature the defects may be frozen into the lattice as has been postulated by Nizboer (98). These oxides may then also be compared to the n-type conductors, but in any case they proved to be practically ineffective catalysts in the temperature range studied.

It may then be concluded that for the single oxides studied, either as the bulk material, or as a skin on a pure metal or flashed metal support, that the most effective catalysts are those in which the metal has a tendency to pass

into a higher valency state, p-type. (In additional support of this it may be noted that non-stoichiometric NiO, i.e. NiO with a large metal deficiency, was 2-3 times more active on first exposure to $H_2O_2$ than stoichiometric NiO, which would have a tendency for less metal ions to pass to the higher valency, i.e. less p-type character. However, in time, and coincident with the stripping of oxygen from the catalyst surface, the "black" oxide became less active and tended to reach the efficiency level of the "green" material. This may interpreted as being due to the system becoming less p-type with the loss of oxygen from the catalyst surface, there then being fewer metal ions in the $Ni^{3+}$ state with, in consequence, a smaller concentration of quasi-free positive holes.)

Following the p-type oxides we have those containing a metal excess accommodated in interstitial lattice positions, CdO, ZnO etc., and lastly those oxides that are commonly termed insulators, MgO, $\alpha$-$Al_2O_3$ etc., which only become measurably active at low temperatures when treated by some means which might be assumed to make them at least superficially n-type semi-conducting.

(3) The nature of the catalyst surface.

The activity series discussion of section (2) would not be complete without referring to the question of the nature of the actual sites on the catalyst surface which may act as a trigger in initiating the decomposition.

We must of course assume that the $H_2O_2$ molecule is adsorbed in such a way as to involve the bonding of the molecule, or that it reacts with a reactive species already adsorbed in such a way as to initiate a chain of reaction steps leading to decomposition and regeneration of the initial reactive species. The nature of the active oxides suggests that electron interaction between molecule and surface, or specific surface site, is the important criterion.

In the more straightforward case of catalysis by metals an analogous situation exists, and much success has attended the theory of Dowden (128) who suggested that in reactions involving chemisorption on metals, the degree of completion of the metal d band was an important factor in deciding the activity. This theory received experimental support mainly in work by Dowden and Reynolds (17), and Couper and Eley (127). Later, Trapnell (129) concluded that chemisorption employed the metal d band with all gases ($C_2H_4$, $N_2$ CO etc.) except oxygen; and that d-character was therefore unlikely to be important in catalytic oxidation reactions, where the metal work function or electron donating property would control the rate.

The position regarding chemisorption on metal oxides is more complex and does not permit any quantitative relationship to be formulated without reference to a particular system. Nevertheless, the interaction of the adsorbed molecule with electrons or electron defects associated with the oxide lattice has come to be recognised as an important factor here. Thus, Gray and Darby (130) consider the adsorption of oxygen on NiO to occur preferentially on metal ions involving electron transfer from the ion to $O_2$ giving $O^-$ or $O^{2-}$ with the setting up of a positive hole. In this instance a more complete transfer of the electron to the adsorbed species is postulated. In the language of semi-conductor theory the electron is trapped by the surface defect.

Volkenshtein (79) recognised the importance of surface defects in determining the activity of chemisorption sites and this theory was later extended by Boudart (131) and Weisz (132) into a more general picture of the electronic nature of the whole surface. Taylor and Thon (133) postulated that only one type of active centre was responsible for a given catalytic reaction, and that this consisted of

a dissociatively chemisorbed species of only one reactant of the system. The reaction then took place through the interaction of one adsorbed reactant and an unadsorbed species; similar to the mechanism outlined by Twigg (134) for the catalytic oxidation of ethylene, in which he considered chemisorption of oxygen alone was necessary; the reaction proceeding between a chemisorbed oxygen atom and a van der Waals adsorbed molecule of the substance being oxidised.

Whilst the Taylor/Thon theory presents a novel approach, it would appear to be unwise to suggest only one type of "active centre". Until further evidence is forthcoming it will be assumed that adsorption may occur at various types of locations on the surface, where radicals or radical ions such as $O^-$ or $O_2^-$ (in the present work) may be associated with different chemical forces according to their environment. Consequently, the "active sites" will not have a uniform activity, even although only one species is preferentially chemisorbed. In addition, as has been pointed out by Laidler (135) the Taylor/Thon theory does not take into account the variation of activation energy with coverage of adsorbate which is well known experimentally from the work of Roberts (136) and of Trapnell (137).

As can be seen from the above discussion no single picture of the nature of a catalyst surface, and in particular of "active centres", has yet been adequately formulated. Each theory has its merits, but needs to be carefully applied in the light of the reaction being studied.

The present results have shown a variation of activation energy with temperature. In the case of the metal/metal oxide catalysts, especially, the activation energy appeared to increase as the temperature of the surface, from which the T change was made, increased. Thus, for example, with $Cu/Cu_2O$ the

following results were obtained (Fig. 13):-

| T. Change | $E_A$ (K. cals/mol) |
|---|---|
| 76 - 58°C | 13.2 ± 0.5 |
| 58 - 100°C | 11.8 ± 0.5 |
| 100- 38°C | 13.4 ± 0.5 |

and with $Fe/FeO/Fe_2O_3$ (Fig. 23).

| T. Change | $E_A$ (K. cals/mol) |
|---|---|
| 101 - 130°C | 16.5 ± 0.5 |
| 130 - 100°C | 21.8 ± 0.5 |

These results cannot be entirely due to the intervention of variable heats of adsorption factors at the different temperatures because of the fast temperature changes, which would have the effect of "freezing" the adsorbate coverage at any one T. In any case since the reaction is 1st order the coverage would be small and would probably give little more variation in experimental $E_A$ than ± 0.5 K.cals/mol in the range studied. So that the phenomena cannot be explained on this basis.

Since it is not just a temperature range that gives a variation in $E_A$, as found for example by Smith and Taylor (138) for the $H_2/D_2$ exchange on ZnO, but a change which is connected with the temperature at which the surface is prepared; then it must be that a surface property is affected by a conditioning process at the various temperatures. In other words, the catalyst may be visualised as having an irregular distribution of adsorption sites on its surface which will vary in activity and importance with the surface temperature. We may also consider the sites to be of varying $E_A$ as has also been postulated by Roginskii and

Tselinskaya (139) to explain results for the oxidation of CO on $MnO_2$.

This is not to say that drastic alterations of the surface are envisaged, since at the temperatures under consideration (38 - 183°C) ionic defects are not very mobile. Rather, it is considered that the adsorbed species may alter in its environment at the various temperatures, and so we may envisage an adsorption distribution over the surface which in its entirety may be located at some time or other at positions approximating to the whole surface, but which at a definite fixed temperature will aggregate at certain locations, or at certain "active sites", and will be associated with the variable chemical forces exerted at these sites.

It would be difficult to identify precisely the exact nature of these "active sites" but for the moment we will consider them to be positions where electron exchange is favourable, such as one of the numerous types of electronic defects existing in an oxide lattice. Thus we may have:-

(1) An excess electron trapped at the surface in various ways.
e.g. at a vacant anion site - constituting an F - centre, or on excess oxygen, or impurity of higher valency metal or lower valency non-metal.

(2) An electron deficiency or p-hole held on a surface cation vacancy, or at an impurity, or excess anion at the surface, or impurity of lower valency metal etc.

At the first type of defect we may have an adsorbed species or a located reaction cycle which can use the electron. The electron is presumed to be "borrowed" by the adsorbing system. In this picture the energy of activation of the process may be limited by the availability of the electron - by the energy required to raise the electron from its electron trap. Generally speaking oxides which are n-type conductors, and therefore in which trapped surface electrons

may predominate as defects, do not free these with energies less than 20-40 K. cals. Thus ZnO surfaces contain F-centres from which electrons will only be released by about 30-40 K.cals of energy (7). At the same time the vacant anion sites which form the electron traps are just the kind of surface defect which would be rapidly poisoned by an OH or O atom "lowering" itself into the vacancy and more firmly or permanently trapping the electron. This poisoning is a very typical feature of n-type catalysis especially on ZnO which may be a "purer" example than $Fe_2O_3$ or CuO.

At the second type of defect we may more usually have a p-hole held in the vicinity of an electron attracting adsorption species (e.g. O or $O_2$), and it becomes the adsorbed species which controls the reaction. During catalysis this species may be replaced by another, and the properties of the defect may as a result change, but poisoning should not be so complete as with the n-type oxides.

(4) The decomposition mechanism and over-all rate controlling factors.

For the catalytic process itself, i.e. assuming a constant surface, the following general reaction steps can be postulated one of which may be rate controlling.

(1) Diffusion of $H_2O_2$ to the catalyst surface, in the gaseous phase or through a stagnant film at the surface.

(2) Adsorption of $H_2O_2$ on the surface.

(3) Reaction, which may be a complex process involving many steps any one of which may be rate determining.

(4) Desorption of products from the catalyst surface.

(5) Diffusion of products into the gas phase.

Processes (1) and (5).

Diffusion is often the rate controlling factor in solid/fluid interface

reactions when the velocity of fluid flow is the factor determining the over-all rate at which the product is obtained. For example, the classical work of Tu, Davis and Hottel (140) showed that the rate of combustion of carbon spheres in air was transport controlled for certain gas flows. Later Katz, Riberdy and Grant (141) found evidence of diffusion control in the catalytic oxidation of carbon monoxide by silver permanganate. Pure Ag $MnO_4$ in the dry state was only slightly active towards CO but on adding water vapour the reaction was accelerated, and the rate constant was found to vary with temperature in a manner typical of a diffusion controlled reaction. However, due to the complexity of this system, it would seem equally plausible to explain the change of $E_A$ with temperature either as being due to diffusion through a water vapour barrier at the surface, the relative humidity was 80%; or to the blocking of some active sites by the water vapour which may condense in the low temperature ( - 3 →11°C) region where the small $E_A$'s are found. Recently, Satterfield, Resnick and Wentworth (142) have found evidence for a transport controlled process by following the variation in Reynolds number of a mixed $H_2O/H_2O_2$ vapour system flowing through an unspecified catalyst cylinder in the temperature range 230 - 500°C. The experiments were conducted on a pilot plant scale.

Diffusion control implies that the reaction at the phase boundary occurs extremely rapidly so that its rate does not affect the observed velocity of the reaction. This would mean that the free energy of activation is low, or that the reacting molecular species are already in an activated state.

In addition, if diffusion is the most important rate determining factor, it is to be expected that the observed velocity obeys the equation for first order kinetics, diffusion being a first order process. Finally, if transport control

is important the temperature coefficient should be approximately equal to the temperature coefficient of diffusion.

The present results show that with the chosen experimental conditions, up to four-fold variations in the flow rate caused no change in the rate of destruction of $H_2O_2$. Now, the reaction is first order with respect to $H_2O_2$ concentration, and following the treatments of Zimmerman (143) and Riddiford (144), for the chemical reaction at the interface:-

$$\text{Rate} = - \frac{d(H_2O_2)}{dt} = k_c C_1 \qquad \text{(i)}$$

where $C_1$ = Concentration of $H_2O_2$ at the interface

$k_c$ = Chemical rate constant.

For the transport process,

$$- \frac{d\ (H_2O_2)}{dt} = k_t\ (C - C_1) \qquad \text{(ii)}$$

$C$ = Concentration of $H_2O_2$ far removed from surface.

$k_t$ = Transport process rate constant.

From Nernst theory,

$$k_t = \frac{\text{Diffusion coefficient of gas}}{\text{Thickness of diffusion layer.}}$$

Eliminating $C_1$ from (i) and (ii) we have :-

$$- \frac{d(H_2O_2)}{dt} = \frac{(k_t k_c)}{(k_t + kc)} \cdot C$$

which is a first order equation giving the reaction rate in terms of the combined chemical and transport rate constants. If the rate of reaction, $- d(H_2O_2)/dt$, is independant of flow rate with C constant (as has been shown in experimental

section), then:-

$$\frac{k_t . k_c}{k_t + k_c} = \text{Constant},$$

for a given temperature which means that $k_t \gg k_c$ and the observed rate is determined by the rate of the chemical process.

In addition, the temperature coefficients of the reaction rate show wide differences in value from 4 to 34 K.cals/mol, depending on the oxide surface. Thus gas-phase diffusion cannot be considered to be a major factor in this catalytic process involving a fast passage of gas molecules over a catalyst surface. Nevertheless, the possibility cannot be entirely neglected in the case of the more active oxides especially the $Mn_2O_3$ spinel series, with $E_A$'s of 4-6 K.cals/mol, where, although the reaction velocity was again independant of flow rate, $k_c$ may not have been so very much less than $k_t$.

Processes (2), (3) and (4).

The reaction involves the transference of a gas-phase $H_2O_2$ molecule to a catalyst surface from whence it is evolved only as products. We may represent the overall process as

$$H_2O_2\ (g) + M = H_2O_2\ (\text{ads.}) \qquad (1)$$

$$pH_2O_2 \qquad m \qquad m'$$

where the relevant activities are given below each species, and

$$H_2O_2\ (\text{ads.}) = \text{products} + M \qquad (2)$$

This is for non-dissociative adsorption. The more rational layout would be:-

$$H_2O_2\ (g) + 2M = \underset{m''}{2\ HO\ (\text{ads.})} \qquad (3)$$

and $2HO\ (ads.) = \text{products} + 2M$ (4)

In support of this we may mention the fact that $O_2$ is believed to dissociate on adsorption on oxides.

Between (3) and (4) we may interpose the steps:

$$HO\ (ads.) + H_2O_2\ (g) = HO_2(ads.) + H_2O \quad (5)$$

$$HO_2(ads) + H_2O_2\ (g) \xrightarrow{m'''} HO\ (ads.) + H_2O + O_2 \quad (6)$$

which would have the effect of increasing the decomposition. If in all these cases we can assume the total active sites to be only slightly covered,

i.e. $m' \simeq 1$ we obtain, for (1) and (2)

$$\text{Rate} = k_2 m' = k_1 pH_2O_2 \quad (7)$$

or (3) + (4) $$\text{Rate} = k_3 . pH_2O_2 \quad (8)$$

but if we allow (5) and (6) to intervene

$$\text{Rate} = k_3\ pH_2O_2 + k_5 m''\ pH_2O_2 + k_6 m'''\ pH_2O_2 \quad (9)$$

We may also assume, reasonable enough, that $m'' = m'''$. Then (3) and (4) give, a steady state, no matter how much (5) and (6) contribute to the decomposition,

$$m'' = m''' = k_3^{\frac{1}{2}} . pH_2O^{\frac{1}{2}} . m \quad (10)$$

If the decomposition is almost wholly due to (3) and (4), (9) reduces to (8), but if the steps (5) and (6) are mainly responsible, (9) is modified by (10) and the assumptions with regard to m'' and m''' lead to

$$\text{Rate} = k_{5,6}\ k_3^{\frac{1}{2}}\ pH_2O^{3/2} \quad (11)$$

If reaction between gaseous and adsorbed $H_2O_2$ is a valid process, i.e. a combination of steps (1), (2), (5) and (6), a second order dependance on $pH_2O_2$ would be expected. Since neither of these latter situations has ever been met with in this work we may rule out the processes which lead to them.

If now we wish to allow for a situation in which m is not equal to 1, i.e. coverage of the active surface by adsorbed species is appreciable, it is necessary to apply the Hinshelwood - Langmuir treatment assuming only that in the steady state m' (and m'', m''' etc.) are constant.

The simplest case (1) and (2) is then modified by considering (1) to be at equilibrium (constant = K), and m and m' to be related by $m + m' = 1$. We then have:-

$$m' = \frac{KpH_2O_2}{1+KpH_2O_2} \qquad (12)$$

$$\text{and, Rate} = \frac{k_2KpH_2O_2}{1+KpH_2O_2} \qquad (13)$$

Quite classically this reduces to (7) with the added information $k_1 = k_2K$, at low coverage and gives a zero order law:-

$$\text{Rate} = k_2 \qquad (14)$$

at high coverage. The case of dissociative adsorption followed by reaction (4) reduces to identical laws (with appropriately changed constants) in the limiting cases. The general case is:-

$$\text{Rate} = \frac{k_4 . K . pH_2O_2}{\left(1+\sqrt{KpH_2O_2}\right)^2} \qquad (15)$$

whence $k_3$ is seen to be equal to $k_4K$.

Intervention of (3) and (4) gives a similar expression in the general case with the restriction $m'' = m'''$, that is:-

$$\text{Rate} = \frac{k_{5,6}.K^{\frac{1}{2}}.pH_2O_2^{3/2}}{1+K^{\frac{1}{2}}.pH_2O^{\frac{1}{2}}} \qquad (16)$$

Since the limiting conditions here give, as before, orders either unity or greater than unity, it is still necessary to set/reject the schemesupon which they rest.

The general conclusions from these elementary theoretical considerations are:-

(1) A first order relation between $H_2O_2$ and surface sites seems most likely. That is against dissociative adsorption.

(2) If dissociative adsorption occurs there must be a second order reaction between adsorbed species to control the decomposition. This seems unlikely in view of the very rapid decomposition.

(3) Gas/surface reactions like (5) and (6) seem disfavoured.

So far we have not considered how the roles of $O_2$ in accelerating, and $H_2O$ in depressing, the rates of catalysis are to be explained.

We may now consider in some greater detail the nature of the stage (2) in the rate process in terms of a given oxide - a p-type oxide such as NiO.

The surface will consist of $Ni^{2+}$ and $O^{2-}$ ions with a two to one ratio of $Ni^{3+}$ ions and vacant cation sites. Now, the $H_2O_2$ may be adsorbed by electron transfer at a metal ion in which case the decomposition may be initiated thus:-

$$Ni^{++} - - - - - - - H_2O_2 = Ni^{+++\ominus} - - H_2O_2^- \qquad (17)$$

$$Ni^{+++\ominus} - - - - - - H_2O_2^- = Ni - - - OH^- + OH \qquad (18)$$

where ⊕ represents a newly created positive hole. This is similar to what would occur with adsorption of oxygen. We could also write thus:-

$$Ni^{++} - - - - - - - H_2O_2 = Ni^{++\oplus} + OH + OH^- \qquad (19)$$

and may perhaps consider the possibility of:-

$$Ni^{++\oplus} + H_2O_2 = Ni^{++} + H_2O_2^+ \qquad (20)$$

followed by:-

$$H_2O_2^+ + O^{2-} = OH^- + HO_2 \qquad (21)$$

In a study of the decomposition of aqueous $H_2O_2$ ($O^{18}$ labelled) by $MnO_2$ and $Fe_2O_3$ etc. as catalysts, Dole et al. (145) showed that the results obtained were consistent with an O-O bond fracture only. There is no reason to suspect that this would be different in the gas phase, and reactions (20) and (21) would then appear to be unlikely. Reactions (17) and (18) are similar to (19) only differing in that electron transfer takes place before dissociation in (17), and in (19) coincides with dissociation. It is doubtful if these two processes can be adequately separated. They are both types of surface oxidation, and, as we show below, it is doubtful if this occurs to an appreciable extent.

In a different scheme, the $H_2O_2$ may adsorb on an electronegative species on the surface such as a vacant cation position an $O^{2-}$ ion or pre-adsorbed species such as $O_2^-$, $O^-$ or $OH^-$ held in the neighbourhood of quasi-free positive holes. Decomposition at an $O^{2-}$ lattice site can be considered to be unlikely energetically, and it would appear that the interaction between a vacant cation site and a peroxide molecule would be insufficient to cause bond fission. Thus, the reaction may be considered to initiate at an $O_2^-$ or $O^-$ pre-adsorbed species;

an adsorbed OH radical will have a transient existence but may be of importance in a chain propagation mechanism. Thus the initiation step may be represented as:-

$$O_2^- \text{ (ads.)} - - - - H_2O_2 = O_2(g) + OH^- \text{ (ads.)} + OH\text{(ads.)} \qquad (22)$$

$$\text{or } O^- \text{ (ads.)} - - - - H_2O_2 = \tfrac{1}{2}O_2(g) + OH^- \text{(ads.)} + OH\text{(ads.)} \qquad (23)$$

These reactions are considered to be entirely surface ones and would contribute little to the crystal lattice disorder, since at low temperatures diffusion into or from the bulk will be slight. They are of course, surface reduction reactions.

Experiment has shown that with "black" NiO, oxygen is stripped from the surface so that the catalyst becomes a murky green. In step with this, the catalyst slowly loses efficiency. Some of the surface oxygen on the other p-type catalysts may also be stripped in this same manner during the course of the reaction. It may perhaps interchange with peroxide oxygen. Furthermore, it has been shown that the presence of oxygen in the gas stream increases the reaction rate, perhaps by adsorbing on the catalyst surface, as $O_2^-$ or $2O^-$ and creating positive holes in the neighbourhood, thus making more sites available at which reactions (22) and (23) may then occur. These steps, (22) and (23), must be considered to be as important as (17), (18) and (19) since increasing the partial pressure of oxygen over a surface containing $Ni^{2+}$ ions should be such as to yield $Ni^{++\oplus}$ ions as well as negatively charged oxygen sites.

Once the decomposition has been initiated giving OH and $OH^-$, their fate has to be decided, and doing so formulates the propagation steps. These species are not considered to be chemically bound at the surface for this would give rise to slow build up of hydroxides. However, this is not to say that the interaction

of OH and $OH^-$ with the surface can be neglected, rather we may regard $OH^-$ and OH as being in a very reactive state held to the surface by weak electrostatic and van der Waals forces, respectively; especially in the case of the high activity p-type oxides, some of which do not form stable hydroxides. (e.g. Cu, Ag).

Considering first the reactions of OH we have the possibilities:-

$$OH\ (ads.) + Ni^{++} \rightleftharpoons OH^-(ads.) + Ni^{+++} \qquad (24)$$

for dissolved and solvated species rather than adsorbed, this would have $\Delta G = -10K.cals$ and $\Delta S = -60$ cals. (Evans, Hush and Uri, 14), and we may consider the error involved in using these values for the adsorption process as being small if it is considered that the solvation influences are replaced by the surface effect of the adsorption forces. This is therefore a highly feasible process but not such that the surface activity of OH would be entirely negligible. Thus, if the fraction of the surfaces covered are used for activities and if ten per cent of the surface Ni ions are present as $Ni^{3+}$, this value of $\Delta G$ gives the ratio of $OH^-$ to OH as approximately $10^{-7}$ at 25°C, but rather more than $10^{-3}$ at 100°C owing to the large entropy change.

Such amounts of OH would be quite enough to permit chain reaction steps to be based on this species.

Thus the OH may react:-

$$OH\ (ads.) + H_2O_2\ (ads.) = \begin{cases} HO_2\ (ads.) + H_2O\ (ads.) & (a) \\ O_2^-\ (ads.) + H_3O^+\ (ads.) & (b) \end{cases} \qquad (25)$$

$$OH\ (ads.) + O_2^-\ (ads.) = OH^-\ (ads.) + O_2\ (g) \qquad (26)$$

$H_3O$

$$\Delta G = -61\ K.cals.$$

Reaction (26) would be similar to one in which electron transfer takes place from $O^-$ (ads.) on the catalyst surface. The $HO_2$ produced in (25a) may then react:-

$$HO_2 \text{ (ads.)} + OH^- \text{ (ads.)} = H_2O \text{ (ads.)} + O_2^- \text{ (ads.)} \qquad (27)$$

or $$HO_2 \text{ (ads.)} + H_2O_2 \text{ (ads.)} = H_2O \text{ (ads.)} + HO \text{ (ads.)} + O_2(g) \qquad (28)$$

(25b) or (27) involves the regeneration of $O_2^-$, and could thus explain a cyclic catalytic process via (22), (25a) and (27); (28) provides the possibility of a short chain reaction. Desorption of $O_2$ is accomplished in the reactions (22) and (23), in which $O_2^-$ or $O^-$ is replaced by $OH^-$ with OH adsorbing on an adjacent site. In this scheme so far, we depend on reaction (27) or on migration of $H_3O^+$ from 25(b) for the removal of $OH^-$ (ads.). It must be noted that $OH^-$ (ads.) may be less labile than $O_2^-$ and $O^-$, and the steady replacement of $O_2^-$ or $O^-$ by $OH^-$ may result in a slowing down of catalysis. Thus, this may correspond with the fall in the catalysis rate on first exposure, or whenever the $H_2O_2$ concentration is raised. We may, however, consider the possibility of the following reactions:-

$$OH^- \text{ (ads.)} + H_2O_2 = HO_2^- \text{ (ads.)} + H_2O \qquad (29)$$

followed by:-

$$HO_2^- \text{(ads.)} + H_2O_2 = H_2O + O_2(g) + OH^- \text{ (ads.)} \qquad (30)$$

Such reactions may be said to occur in solution as, for example, in the slow decomposition of concentrated $H_2O_2$ by alkali. They may, however, require that $OH^-$ (ads.) should be in a specially reactive state.

Finally we have to consider desorption of $H_2O$ and other possible reactions of $HO^-$ and $HO_2^-$. Desorption of $H_2O$ is probably very rapid and the reaction:-

$$2OH^- = O^{2-} + H_2O \qquad (31)$$

which will follow the formation of any hydroxide lattice is really a matter of oxide growth. The same may be said of the possible step:-

$$2HO_2^- = O^{2-} + O_2 + H_2O \qquad (32)$$

which has been shown by McFadyen (81) and Nettleton (96) to occur at a rate negligible compared with that of catalysis (1 to 1000 on $Cu_2O$ at 100°C). This is true also for:-

$$HO_2^- + HO^- = O^{2-} + H_2O_2 \qquad (33)$$

Also, as we have seen for NiO (black), $H_2O_2$ tends to reduce the normal p-type surface, a well-known phenomena which already had been recognised in 1863 by Brodie (146), so that these reactions are unlikely to be important compared with:-

$$HO_2^- + OH^- = H_2O + 2O^- \qquad (34)$$

followed by:-

$$2O^- + H_2O_2 = O_2(g) + 2OH^- \qquad (35)$$

as a propagation step, or at high temperatures, we could consider the oxygen desorption:-

$$2O^- + 2\,Ni^{++\oplus} = O_2(g) + 2\,Ni^{++} \qquad (36)$$

as a terminating step.

The key to the mechanism is probably to be found in the disturbance of the surface equilibrium which any sudden change in $H_2O_2$ concentration must bring

about. Thus, as a result of (23) or (24) and (25) $O_2^-$ or $O^-$ is steadily replaced by $OH^-$. This need not necessarily affect all the adsorbed oxygen but only the most labile part. When the change is complete the electron balance in the surface layers of the oxide will be disturbed resulting in a slight rearrangement of electronic defects which will tend to reach an equilibrium position. This process will depend on diffusion in surface layers and would be very slow, although much faster than bulk diffusion.

We have, of course, shown experimentally that the reaction is first order w.r.t. $H_2O_2$ and how oxygen and water vapour affected the rate of the reaction. Raising the oxygen pressure increased the rate. This could be explained by the surface concentration of oxygen being increased to come to equilibrium with that of the gas phase. New sites of $O_2^-$ and, or $O^-$ would be created which would influence the original electron transfer step. On the other hand, increasing the partial pressure of $H_2O(v)$ decreased the rate, perhaps by retarding reactions (27) and (28) which will reduce the speed with which sites will become available by prolonging their occupancy with $OH^-$.

On this basis it is highly probable that the rate controlling step on the p-type catalysts is the original electron transfer to the substrate, and the over-all velocity of the reaction will be dictated by the availability of these electron sources or "active sites".

In the above no commitment was made as to the exact source of the electron ($O^-$, $O_2^-$, $M^{++}$). However, this question has been extensively studied by Hart and McFadyen (81) with films of $Cu_2O$ on copper. They concluded that the original electron transfer takes place at low temperatures from a pre-adsorbed $O_2^-$ ion rather than $O^-$ or $M^{++}$. They based their argument on ther-

modynamic considerations using data from Evans, Hush and Uri (14), but also on the results of Garner and coworkers (44, 45, 46, 47) which suggest that $Cu_2O$ oxide surfaces will be covered at temperatures of the order of 50°C with oxygen in the $O_2^-$ form. Further, this work suggests that plain desorption of oxygen is always a slow process, which, as we mention elsewhere, may explain why $N_2O$ catalysis, requiring as it does the straight desorption step, is so much slower than $CO/O_2$ catalysis or $H_2O_2$ decomposition. $CO/O_2$ (see Section I equation (6) ) requires no desorption at all, while in the present scheme $O_2$ is liberated in a replacement. It would be less easy to postulate this with $O^-$ as the relevant species.

Of course, the position and reactivity of the $O_2^-$ will affect the energy of activation. The surface condition with regard to adsorbed oxygen will change markedly in the region 38 - 183°C in which the experiments were conducted. At 100°C and above oxygen is readily desorbed; the $O_2^-$ species has therefore a short life. At the higher temperatures it must be expected that only the most firmly held oxygen will be effective, and these may invoke a higher energy of activation. At the higher temperatures still, the $M^{++}$ ions may act as electron donors.

The disappearance at temperatures above 100°C of an activity fall cannot be readily ascribed to steps like (32) because of the very high decomposition. Reactions (29) and (30) may again be invoked. This suggests that whereas the only reaction by which $OH^-$ (ads.) may further the catalytic process at low temperatures is (27) and (28), it may be attacked by $H_2O_2$ directly at higher temperatures and it therefore loses its relative passivity.

In reactions (25) and (28) we have the possibility of chain decomposition

initiated by an active OH radical produced at the surface in (22). The surface reaction is, of course, a chain reaction in which the active surface centres are the carriers. Thus the production of active radicals, themselves capable of continuing a chain, is a branching of the surface process. Reactions (22), (26) and (27) are initiation and propagation steps in the normal surface - centred chain. There is no termination stage in the surface - centred chain but, in the radical branch, mutual interactions between radicals may be regarded as terminating. The branch is itself a straight chain, and no further branching can be postulated. It may be considered as proceeding within the orbit of the surface chemical forces, i.e. within the chemisorbed layer or within the van der Waals layer. The latter is preferred.

Whether or not the bulk of the decomposition proceeds via the chemisorbed layer chains, it must be clear that the catalyst owes its effect to ability to donate and accept an electron readily. Thus we would appear to have a reason why the n-type and insulator oxides are much poorer catalysts than $Cu_2O$, $Ag_2O$, etc.

It should be noted that the value of $7.0 \pm 0.5$ K.cals/mol found as the $E_A$ for "green" NiO is similar to the value of 7 K.cals/mol found by Wright and Andrews (147) for the surface energy level of electrons in NiO. Whilst the value of $12 \pm 1$ K.cals/mol found for a $Cu_2O$ surface is similar to the value found by Rideal and Wilkins (148) for the $E_A$ of surface conductivity in this oxide (9.5 K.cals/mol). It may be considered that surface conduction will involve similar electronic forces as those involved in adsorption.

For an n-type semi-conductor such as ZnO, the surface in equilibrium with oxygen will consist of $Zn^{2+}$, $O^{2-}$ ions and vacant anion sites balanced by quasi - free electrons; excess metal being accommodated in interstitial positions.

In certain instances the anion vacancy contains a trapped electron forming an F - centre. In this case it is unlikely that reaction will proceed by electron transfer from a $Zn^{2+}$ or $O^{2-}$ ion, or even from $O^-$ (ads.) - since the tendency is to lose not adsorb oxygen, but it may be that an $H_2O_2$ molecule adsorbed in the vicinity of an F-centre could initiate decomposition by accepting an electron, thus:-

$$H_2O_2 - - - - - (v.a.s.)^- = HO\ (ads.) + OH^-(ads.) + (v.a.s.) \quad (37)$$

where $(v.a.s.)^-$ = F-centre.

and (v.a.s.) = vacant anion site.

However, this electron will be firmly held as known from the optical properties of ZnO which, according to Seitz (7), give a value of about 40 K. cals for the energy of ionisation from an F-centre in the bulk of the oxide. The value for a surface site would be lower, and perhaps not far from the 34 K.cals which is the $E_A$ of $H_2O_2$ decomposition on ZnO.

Furthermore, this picture permits an explanation for the ready decay of efficiency on a heat treated sample of ZnO during a run. Thus, we may consider that an electron removed from the F-centre to a surface species would be more mobile than before and could eventually be captured by a positive defect (e.g. interstitial $Zn^+$). So that the surface would gradually become stripped of active sites and $H_2O_2$ would have no tendency to replenish these by direct action on the ZnO normal lattice.

The steps following (37) would be similar to those outlined above for the p-type catalysts, namely (29), (30), (26), (25a) and (28).

Clearly, the above argument could not also be applied to the catalysis

on CdO or CuO, since these are better catalysts than ZnO and invoke energies of activation of 12 and 15 K.cals/mol, respectively. At first sight this discrepancy in activity between oxides which are all n-type may be difficult to understand, but in the light of the surface reducing action of $H_2O_2$, the position becomes clearer. With CuO it may be expressed simply thus:-

$$2CuO + H_2O_2 = H_2O + O_2 + Cu_2O \qquad (38)$$

The surface may not be entirely converted to cuprous oxide, but an intermediate $Cu_2O/CuO$ state may be envisaged which may then propagate the reaction in the same manner as the p-type oxides. There was no tendency for this oxide to lose activity during exposure to $H_2O_2$.

The other n-type oxides examined, CdO and $Fe_2O_3$, are similar to CuO, and unlike ZnO, in that the oxides of lower valency are stable. So that we may again postulate surfaces containing $Fe^{+}$ and $Fe^{++}$ metal ions, similarly with CdO. It may be, however, with the latter that the oxygen is stripped from the surface and the excess cadium is accommodated in interstitial positions as atoms or ions, which in itself implies that more electron sources would be available to initiate catalysis.

This connection of catalytic activity of the n-type oxides with the ability of $H_2O_2$ to reduce the surface giving, as it were, a p-n equilibrium can also be used to explain the remarkable fall of catalysis on raising the $H_2O_2$ concentration. For if we reduce the $H_2O_2$ concentration from $C_i$ to $C_i/3$ we ease the surface reduction; the surface then at $C_i/3$ becomes stabilised. Then, the change back to $C_i$ is accompanied by a big drop in catalysis from the original $C_i$ value which may be due to the lack of suitable surface sites on the catalyst conditioned, as it were, at $C_i/3$. This, of course, would not

apply to the p-type oxides since they have an inherent tendency to pass from $M^{+}$ to $M^{++}$ with the adsorption of oxygen, and raising the partial pressure of oxygen in contact with such a surface, i.e. in a change from $C_i/3$ to $C_i$, will only serve to increase the concentration of quasi-free positive holes, and $O_2^-$ or $O^-$ ions, to the original $C_i$ value.

So far we have not touched on the probable mechanism of initiation on the insulator oxides. Experiment showed that in the temperature range studied these were inactive catalysts and only became active when treated in some fashion as may reasonably be held to make them n-type (see section (3) ). The sources of electrons may then be F-centres, or reduced metal ions, or in the case of $Al/Al_2O_3$ as has been postulated by Mott (149) electrons may pass to the surface by a quantum mechanical tunnel effect, while the oxide film is still growing. This being so, it could explain the finding that $Al/Al_2O_3$ when heated in air was non-active (oxide film 80-100$A^{\circ}$ thick), but when subjected to a fierce heat-treatment in hydrogen and quickly cooled; a fairly high catalysis rate was found (oxide film = 40$A^{\circ}$, say). So long as the $Al/Al_2O_3$ was in contact with $H_2O_2$, the oxide film would remain at an intermediate thickness and catalysis would be recorded. However, stopping the $H_2O_2$ flow and leaving the catalyst in contact with air overnight would effectively replace a reducing atmosphere by an oxidising one, which, in time, would allow the catalyst to recover to its original oxide thickness, and no catalysis would be observed on starting up at 180°C, because no electron sources would be freely available to initiate the decomposition. This is not to say that a surface of uniform thickness is visualised but that there will exist active surface discontinuities and cracks which in 24 hours will become, as it were, filled up with an oxide film. This irregular growth of oxide films on aluminium on exposure to air has been

observed by Vernon (150), and it may also be noted here that recent work by Hart (151) has shown that hydrated oxide films of aluminium growing in water are accompanied by intergranular attack.

The results obtained with the insulator oxides were in fair harmony with those of Giguère (34) for Sn and Al surfaces in a static system using $H_2O_2$ vapour concentrations and temperatures similar to those here. The picture is markedly different to the work of Satterfield and Stein (26) who use high partial pressures of $H_2O_2$ and $H_2O$ and find second order kinetics in $[H_2O_2]$ and complex inhibition by $H_2O$ vapour. The influence of increasing partial pressure of oxygen and water vapour in the present experiments was, as described, only just detectable with the "normal" insulators, due to lack of catalytic activity.

(a) Expansion of kinetics.

We may now attempt to complete the general kinetic mechanism approach begun above. The features to be accommodated are:-

(1) the first order dependence on $[H_2O_2]$ for rapid changes of $[H_2O_2]$

(2) the slow response to oxygen pressure changes which follow the approximate relation:- rate of catalysis $\propto pO_2^{1/8}$

(3) the rather more rapid response to $pH_2O$ which poisons according to the relationship:- rate of catalysis $\propto pH_2O^{-\frac{1}{2}}$

(4) the complex changes which follow an instantaneous change of $[H_2O_2]$.

In the first place we may regard the peroxide decomposition as occurring on a surface fixed in composition. This surface is subject to slow change when $H_2O_2$, $H_2O$, or $O_2$ partial pressures are changed separately or together, but we may consider these changes from a kinetic point of view as separate processes.

The fast decomposition process may then be formulated as controlled by:-

$$H_2O_2(g) + S^* = \text{products} + S_1 \qquad (39)$$

where $S^*$ is an active surface species, and $S_1$ is able to return to $S^*$ in a step which is not rate controlling. We have discussed the nature of $S^*$ already. It may be $O^-$, $O_2^-$, $HO^-$ a metal ion, $H_2O_2$ or an $H_2O_2$ dependent species like $HO_2^-$.

We then have from (39)

$$- d\left[H_2O_2\right]/dt = kpH_2O_2\, m_{S^*} \qquad (40)$$

If $m_{S^*}$, the surface activity of this active species, remains constant during a very rapid change in $pH_2O_2$ we get the condition for a first order reaction.

On the other hand we have to observe that a relatively fast change in the catalysis soon sets in after the establishment of a first order relationship. This can only be due to a change in $m_{S^*}$. It may, however, be induced in various ways:- via $H_2O_2$, $O_2$ or $H_2O$. It is too fast to be due to $O_2$ and too large to be due to $H_2O$. Thus it must be due to $H_2O_2$.

A simple possibility is that the surface is at first, at low temperatures anyway, capable of conducting a simple cycle based on $O^-$ and $O_2^-$.

$$O^- + H_2O_2(g) = O_2^- + H_2O(g) \qquad (41)$$

$$O_2^- + H_2O_2(g) = O^- + H_2O(g) + O_2(g) \qquad (42)$$

with either of the reactions rate determining or with a balanced rate.

Then poisoning could occur thus:-

$$2O^- + H_2O_2(g) = 2\,OH^- + O_2(g) \qquad (43)$$

in which $OH^-$ is a much stabler species than either $O^-$ or $O_2^-$.

At high $[H_2O_2]$ we may consider a regenerating step:-

$$OH^- + H_2O_2(g) = O_2H^- + H_2O(g) \qquad (29)$$

which may indeed be balanced so that the poisoning effect of $H_2O$ is excercised here. (44) could be succeeded by the slow step:-

$$\left.\begin{aligned} O_2H^- + OH^- &= 2O^- + H_2O(g) \\ \text{or} \qquad 2O_2H^- &= O_2^- + O^- + H_2O(g) \end{aligned}\right\} \qquad (34)$$

Steps like (43), though quite rapid, are slow compared with catalysis itself, and so for rapid rate changes we could represent the whole process by (41) and (42). These lead directly to a realisation of the importance of $O_2$ which would have an effect on the surface activities of $O^-$ and $O_2^-$, and also on other surface electronic effects. Thus in the oxidation of p-type metals, Wagner and others have found that the rate of growth is proportional to $pO_2^{1/6} - pO_2^{1/8}$. To explain this finding the rate is held to be proportional to the concentration of vacant cation sites, and p-holes - two of which are induced per electron by the oxygen. In our case we may consider that the two singly charged ions $O^-$, the two vacant sites and the two p-holes arising on adsorption of our oxygen molecule - six species in all, can all act as an anchor for a catalytic cycle involving $HO_2$.

Thus we would expect:-

Rate $\propto p{O_2}^{1/6}$, which is sufficiently close to the experimental finding. Equation (41) gives (39) where $m_{S*}$ is now seen to be $m_{O^-}$ (assuming $m_{O^-} = m_{O_2^-}$). The poisoning scheme above may be analysed. At balance, (43) and (34) give:-

$$k_{43} \cdot m^2_{O^-} \cdot pH_2O_2 = k_{34} \cdot mO_2H^- \cdot m_{OH^-} \qquad (44)$$

while the balanced reaction (29) gives:-

$$mO_2H^- = \frac{K_{29} \cdot pH_2O_2 \cdot m_{OH^-}}{pH_2O} \qquad (45)$$

which gives when substituted in (44):-

$$k_{43} \cdot m_{O^-}{}^2 \cdot pH_2O = k_{34} \cdot K_{29} m^2 OH^- \qquad (46)$$

substituting for $m_S{}^*$ (now $m_{O^-}$) in (39) we obtain, when $m_{OH^-}$ is approximately constant (e.g. when $\simeq .1$):-

$$\text{Rate} = k \cdot pH_2O_2 \cdot \left(\frac{k_{34} K_{29}}{k_{43}}\right)^{\frac{1}{2}} \cdot \left(\frac{1}{pH_2O}\right)^{\frac{1}{2}} \cdot$$

$$= k' \, pH_2O_2 \cdot \left(\frac{1}{pH_2O}\right)^{\frac{1}{2}} \qquad (47)$$

Combining this with the oxygen dependence we find

$$\text{Rate} = k'' \cdot pH_2O_2 \cdot \left(\frac{1}{pH_2O}\right)^{\frac{1}{2}} \cdot \left(pO_2\right)^{1/6} \qquad (48)$$

Such an expression is that applicable to changes which are slow enough to allow all slow surface equilibria to settle.

Equation (48) applies only if $m_{OH^-}$ is constant, and this is surely

only likely to be a valid assumption when it is approximately equal to unity i.e. at a highly poisoned surface such as will obtain at a low temperature.

$m_{OH^-}$ from (45) gives:-

$$\text{Rate} = \frac{k' \; p_{H_2O_2}}{p^{\frac{1}{2}}_{H_2O}} \cdot \frac{K_{29} \cdot p_{H_2O}}{p_{H_2O_2} \cdot K_{29} \, p_{H_2O}} \qquad (48a)$$

(since $m_{OH^-} + m_{O_2H^-} = 1$)

This suggests that a zero order rate should come in when $p_{H_2O_2} \gg K_{29} \, p_{H_2O}$ and that under these circumstances:-

$$\text{Rate} \propto p^{\frac{1}{2}}_{H_2O} \qquad (48b)$$

i.e. an acceleration not diminution in rate, which may come in at much higher $H_2O_2$ partial pressures

It should be mentioned that similar rate equations to these may be explained by assuming that the adsorption of the relevant species is governed by either a logarithmic (Temkin and Pyzhev, 160) or a power rate law (Kwan, 161). Kwan (162), for example, applied the power rate law to the $2CO + O_2 = 2CO_2$ reaction on NiO.

The power rate law states that the rate of adsorption of a substance is given by:-

$$\text{Rate} = k_1 p \, \theta^{-\alpha} - k_2 \, \theta^{-\beta} \qquad (49)$$

where p is the pressure of adsorbate and $\theta$ is the fraction of surface covered. Other symbols are constants. At equilibrium this law reduces

to the Freundlich isotherm. For the CO reaction it is necessary to assume a mechanism which Kwan took as:-

$$\theta_2 = 2\theta \qquad (50)$$

$$O + CO = CO_2 \qquad (51)$$

(51) being slow. Then for the reaction:-

$$\text{Rate} = k\, pCO\, \theta_o^{\beta} = kpCO \cdot pO_2^{\beta/(\alpha+\beta)} \qquad (52)$$

which is in agreement with high temperature results provided:-

$$\frac{\beta}{\alpha+\beta} = 0.5$$

an assumption shown to be reasonable by many examples of adsorption rate.

This method of treating surface reactions becomes very complicated when it is necessary to consider several surface species, and consequently several possible interlocked reactions - as in fact we find it necessary to do. It amounts to replacing the surface coverage, $m_x$ in our Scheme, by $m_x^{\beta}$ for each surface reaction. When this complexity has added to it the uncertainty relevant to the numerical values of $\alpha$ and $\beta$ for each species, it seems evident that the treatment is inapplicable. We might however take for illustration our elementary scheme, namely that the rate of catalysis is controlled only by the adsorption step:-

$$H_2O_2 + 2S^* = 2\,SOH$$

and that subsequent reactions are so rapid as to be at equilibrium.

$$\text{Then Rate} = k\, pH_2O_2 \cdot \theta^{-\alpha} \qquad (53)$$

and if $p_e$ is the partial pressure of $H_2O_2$ which would be in equilibrium with the chemisorbed species S.OH.

$$p_e = K.pH_2O \cdot pO_2^{\frac{1}{2}} \qquad (54)$$

from the overall reaction equilibrium.

Also $$p_e = \text{const.}\ \theta^{(\alpha+\beta)} \qquad (55)$$

since the Freundlich type of equation relates $\theta$ and $p_e$. Thus

$$\text{Rate} = \frac{k\ pH_2O_2}{pH_2O^{\frac{1}{2}} \cdot pO_2^{\frac{1}{4}}} \qquad (56)$$

if $\alpha/(\alpha+\beta) = 0.5$

Clearly, although this gives the correct dependence on both $H_2O_2$ and $H_2O$ it fails completely for $O_2$.

To sum up, we may conclude that the prime consideration as to what makes an oxide a good catalyst in this reaction, is its ability to donate electrons to the substrate from labile surface sites.

(b) Initial and cyclic efficiency changes.

It would appear with the metal films that two competitive surface processes are occuring, one dominant at high and the other at low temperatures. This fall in efficiency cannot be due to the setting up of an equilibrium distribution of defects on the surface through migration from the bulk, since at these temperatures (60- 180°C) ionic type defects are highly immobile, and the time lag in attaining the steady value would not be accounted for.

During the course of the reaction parts of the surface may be coveredby intermediate reaction species such as $HO_2^-$ or, and more especially, $HO^-$.

It is not, however, considered that these species are chemically bonded at the surface (for if this were so then the surface would become poisoned) rather that they will propagate the reaction from the van der Waals layer. The initial decay may be due to inactivation proceeding through the stripping of excess active oxygen from the surface, and in support it has been shown that "black" NiO will become a dirty green in about 50 minutes whilst catalysing $H_2O_2$ vapour. This change must involve the slow removal of labile surface oxygen. The excess oxygen will readily oxidise $H_2O_2$ and when the supply is exhausted or has reached an equilibrium, the catalysis will assume a steady rate.

Analysis of the decomposition figures on the NiO and $Cu_2O$ flashed films during the initial fall in catalysis shows that they conform to a law of the type:-

$$\frac{d(D)}{dt} = K. \exp(-AD) \qquad (a)$$

where D is the fraction decomposed at time t; A and K are constants.

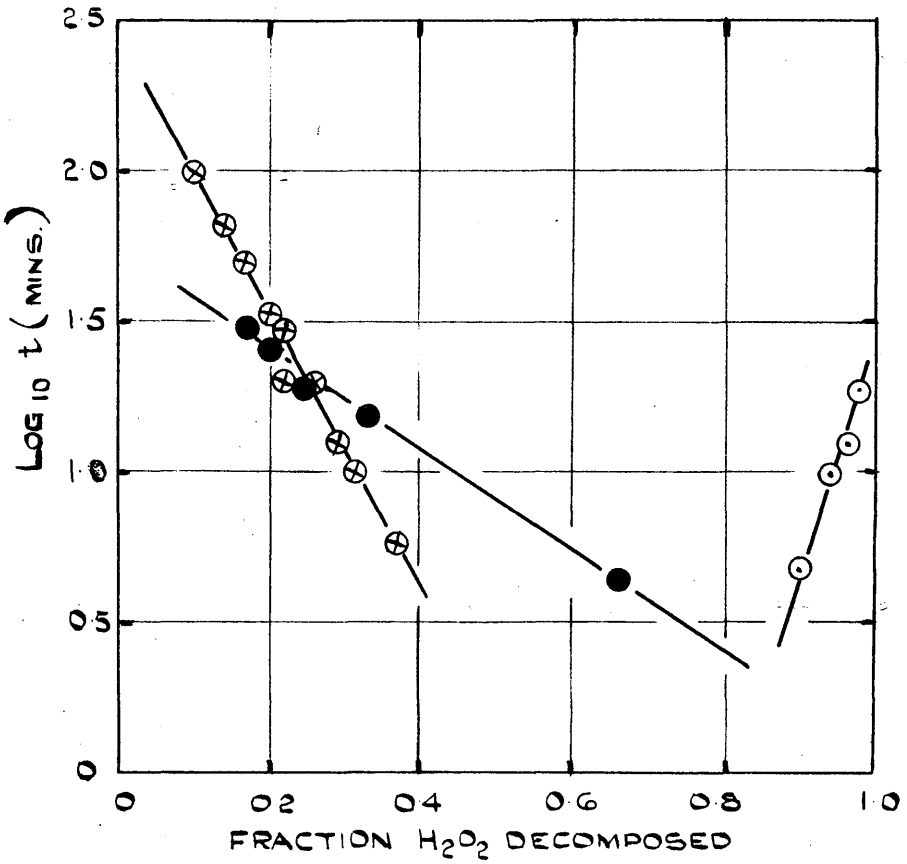
On integration this gives:-

$$D = 1/A.\left[\ln(t+t_o) - \ln t_o\right]. \qquad (b)$$

where $t_o = 1/AK$.

This is a form of the Elovich (163) equation subsequently shown by Taylor and Thon (133) to apply to many catalytic reactions. The value of $t_o$ is generally found by trial and error plots until a straight line is obtained when graphing D against $\ln(t+t_o)$. In the present case when $t_o = 0$ equation (a) may be written:-

$$\log t = (A/2.3)\, D \qquad (c)$$




ELOVITCH TYPE PLOTS OF INITIAL EFFICIENCY CHANGES

⊙ OXIDISED, FLASHED NICKEL FILM AT 160°C. (INCREASE IN EFFICIENCY)

● Ni FILM - 100°C (EFFICIENCY DECREASE)

⊗ " " - 60°C ( " " )

FIG. 51.

and the graph of log t against D should give a straight line. This is shown in Fig. 51 for the slow fall in decomposition of a nickel/nickel oxide flashed film at 60°C, and for the rise and fall of efficiency of a $Cu/Cu_2O$ film at 32°C, before the onset of steady catalysis.

(5) The Arrhenius parameters.

A common criterion in classifying catalytic reactions is the temperature coefficient or activation energy of the reaction. This is calculated from the rate of reaction at different temperatures.

The interpretation of the meaning of the temperature coefficient of a solid catalysed reaction is well-known to be a difficult matter. Recently, Trapnell (152) and Rideal and Trapnell (153) have criticized the significance given to $E_A$ as found from the equation:-

$$\frac{d \ln k_{obs}}{dT} = \frac{E_A}{RT^2} \qquad (1)$$

They suggest that a better indication of catalytic power would be to measure the temperature coefficient at constant surface coverage of reactants.

This criticism is a real and valid one, since in very many cases the figures quoted for experimental activation energies have been those obtained by calculating $E_A$ from the above equation when the reaction had reached a steady value after a temperature change. This complicates the system by the intervention of the heat of adsorption of the reactant. Thus, for a unimolecular surface reaction retarded by one of its products, it may be shown (Hinshelwood, 165) on a simple Langmuirian basis that:-

$$\frac{d \ln k_{obs}}{dT} = \frac{E + \Delta H_1 - \Delta H_2}{RT^2} \qquad (2)$$

where, E = True activation energy of the reaction.

$\Delta H_1$ = Heat of adsorption of the reactant.

$\Delta H_2$ = Heat of adsorption of product which poisons.

and by equating (2) and (3), we see that:-

$$\underline{\underline{Ea = E + \Delta H_1 - \Delta H_2.}} \qquad (3)$$

This expression may, as a first approximation be taken to hold for the present reaction - which is retarded by water vapour. (We are here ignoring for the sake of simplicity, the slight accelerating role of oxygen.) The heats of adsorption $\Delta H_1$ and $\Delta H_2$ will themselves be dependant on the degree of coverage of the surface with adsorbed molecules, even although in a first order process the adsorption is small.

However, as is well known, the degree of coverage of adsorbed molecules changes slowly in time, as has been shown, for example, in the work of Taylor and Liang (154) where the volume of hydrogen adsorbed on ZnO took 16-17 hours to move from 5 to 7 ccs at 184°C. So that the difficulty of this variation in $\Delta H$ may be somewhat overcome by making an instantaneous adiabatic temperature change in which the fraction of surface covered can be held constant. It may quite reasonably be expected to take 20 - 25 minutes before the coverage adjusts itself to the new temperature, which is the average time taken to reach a steady decomposition value in these experiments after a fast temperature change.

In other words, in the present experimental set-up, it is possible by a minor extrapolation to "zero" time to obtain a temperature coefficient at constant adsorbed volume for any given temperature i.e. at a constant $\Delta H_1$ and $\Delta H_2$. Thus, if this condition is achieved the $E_A$ values found with

different catalysts are fairly certain to be significant if they are compared by the values obtained at the same temperature. Since there is no reason to believe that $\Delta H_1$ and $\Delta H_2$ at 100°C, say, will vary much from one catalyst to another of the same activity class. We may then interpret our $E_A$ values on the basis given in section (3).

(6) The compensation effect.

The catalysts examined gave a range of $E_A$ from 4K.cals/mol with $Mn_2O_3$ to 34 K.cals/mol for ZnO. For a single catalyst we find a variation in $E_A$ according to the temperature of determination (e.g. $Fe_2O_3$ gave from 16 to 22 K.cals/mol. between 100 - 130°C) and for NiO catalysts containing trace impurities a variation in $E_A$ was found in determinations at the same temperature.

Now, we write the Arrhenius equation:-

$$\text{Rate} = C_{H_2O_2} \times A \times \exp.\ (-E_A/RT) \qquad (X)$$

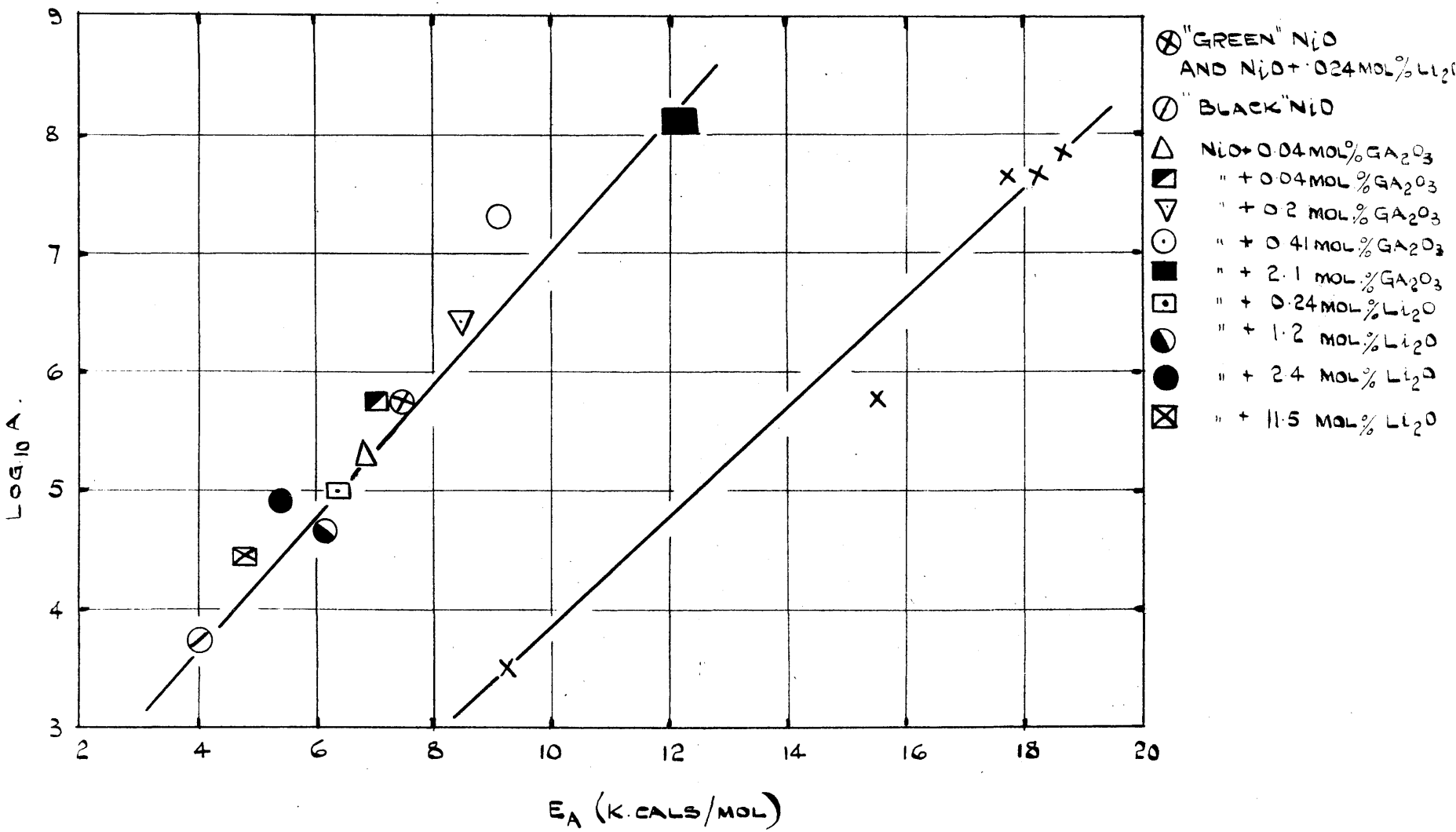
where $E_A$ is the energy of activation and A is the frequency or entropy factor. In the case of NiO + impurities we find, as shown in Fig. 52, that A changes with $E_A$ so that the linear relationship:-

$$E_A = \text{constant.} \ln A + \text{constant}$$

or

$$\ln A = \text{constant.} E_A + \text{constant}$$

is adhered to. Fig. 52 demonstrates this for the reaction on NiO + x mol % $Ga_2O_3$ and NiO + x mol % $Li_2O$. For these series a change in $E_A$ for the temperature drop from 100°C is always accompanied by a similar change in A, and the points lie on a straight line. This figure also shows a similar relationship derived from data given by Parravano (61) for the reduction of NiO (containing $Li_2O$, $Ag_2O$, $Al_2O_3$ etc. as impurities) by hydrogen in the temperature range




"COMPENSATION EFFECT." $Ni_1O$ + TRACE IMPURITIES

X REDUCTION BY HYDROGEN, PLOTTED FROM DATA OF PARRAVANO (61)

OTHER PLOT SHOWS RELATIONSHIP, IN THE PRESENT REACTION, OF $E_A$ AND $LOG_{10} A$

FIG. 52.

150 - 350°C and partial pressures of 200 - 500 mm Hg.

This type of relation has long been observed for heterogeneous systems of this kind. It is called the "Compensation Effect" since, as will readily be seen, a high $E_A$, which would reduce the amount of reaction at a given temperature, is accompanied by a high A which partly compensates.

Barrer (155) has stated that this effect has no deep significance but arises from the fact that practical measurements of rate lie within a narrow range. Thus if in (X) we put:-

$$\text{Rate} = k.\ C_{H_2O_2}$$

so that $$k = A.\ \exp.\ (-E_A/RT).$$

and regard k as substantially constant while T varies over a wide range then:-

$$\ln k = \log A - \frac{E_A}{2.303T}$$

i.e. $$\log A = \frac{E_A}{4.577} + \text{constant}.$$

Such a relationship does fit many series of results e.g. decomposition of $N_2O$ on $Cu_2O$ (Cremer and Marschall, 156) and decomposition of $N_2O$ on $Pt/Al_2O_3$ (Mikovsky and Waters, 157), but it fails when a single promoted catalyst is being considered (Fig. 52), because here k is by no means constant in comparison with $E_A$ and A. Barrer's criticism was intended apparently to apply to ranges of catalysts active over several hundred degrees.

Cremer (158), on the other hand, has argued that the effect has a fundamental significance and has discussed the relation for many systems. (e.g. $N_2O$ decomposition and chlorination catalysis).

We must still, however, explain the change of $E_A$ with temperature and composition of a given catalyst and why A always changes in the direction of compensation. Much of Cremer's discussion is relevant to this question. Thus, although some of the discussion has been about false cases, there is an effect here which is real and worth examining.

There are two sources of variation in the A factor, the concentration of active sites and the entropy term. Thus if we write the effective process as:-

$$H_2O_2 + A \rightleftharpoons (H_2O_2 - - - - A)^* = \text{Products} + A., \qquad (1)$$

where $(H_2O_2 - - - - - A)^*$ represents an intermediate complex which is certainly an adsorbed species, the absolute rate theory would give:-

$$\text{Rate} = k \times C_{(H_2O_2 - - - - - A)^*} \qquad (2)$$

Now, $K = C_{(H_2O_2 - - - - A)^*}/C_A . C_{H_2O_2}$

and $K^* = \exp. (-\Delta G/RT)$

so $\text{Rate} = k . C_{H_2O_2} . C_A . \exp. (-\Delta G/RT).$

and if also $\text{Rate} = k_1 . C_{H_2O_2}.$

$$k_1 = kCA. \exp. (\Delta S/R). \exp. (-\Delta H/RT).$$

Also, if we as usual write the velocity constant in the Arrhenius style:-

$$\frac{d \ln k}{dt} = \frac{E_A}{RT^2} \qquad (Y)$$

we easily find:-

$$k_1 = ke\ C_A \exp.\ (\Delta S/R) \exp.\ (-E_A/RT).$$

(Y) in the form $k = A \exp.\ (-E_A/RT)$.

shows that the A factor has two variable parts $C_A$ and $\Delta S$.

Now, for an adsorption process we would not expect $\Delta S$ to vary much since it involves, no matter what the solid, largely the same type of process as the condensation of a gas molecule. It will, however, vary slightly according to whether the $H_2O_2$ is held firmly or in a mobile surface state. We conclude that $C_A$ is the main cause of A variation.

A further point is that reaction (1) and hence equation (2) refer to a single process on a single type of active site, but we may be dealing with a range of processes each with a different $E_A$ and $C_A$. (Thus the effect of a temperature change would be similar to the effect of temperature on conductivity in a semi-conductor with a number of different kinds of impurity. The over-all rate would be in the form of a series:-

$$k = k'.\ C'_A.\ \exp.\ (-E'_A/RT) + k''\ C_A''\ \exp.\ (-E''_A/RT) + \text{etc.}$$

(7) Catalysis on NiO and promoted NiO.

In previous sections reference has been made to some of the catalytic results found with the nickel oxide system. In addition, the results section described certain structural properties which have been investigated. In view of the special attention given to NiO in this work this section will deal with the results obtained in greater detail.

The catalysis was examined on flashed Ni films, specpure Ni metal and

"black" and "green" NiO. At 100°C, "black" NiO gave 87% decomposition falling to a steady value of 63% after 55 minutes, "green" NiO gave 50% steady decomposition, specpure metal 12% and flashed film 20-22%., The flashed film cannot be strictly compared with the others because the result refers to a different flow system. The activities may then be placed:-

"black" NiO > "green" NiO > Ni/NiO,

Here, as in most cases where metal/metal oxides and bulk oxides of the same element were examined, the bulk material was more active.

The higher activity of "black" over "green" nickel oxide, and the loss of efficiency in time of the former, was probably due to the excess oxygen which this oxide contains. It may be considered that the loss in activity which occurs in step with the colour change is due to the stripping of the labile oxygen from the catalyst surface. This oxygen is chemisorbed, but loosely bound (Hauffe and Engell, 159) and the onset of the steady decomposition level may be coincident with the setting up of a less active surface where the oxygen content is at equilibrium with that in the gas phase. In which case, all the labile oxygen is not removed and there still exists appreciable deviation from stoichiometry - the colour did not fully become the apple green of stoichiometric nickel oxide. The colour of the oxides containing more than 0.5 mol % $Li_2O$ in "green" NiO was unmistakably black but no loss of catalytic efficiency nor change of colour was observed, with passage of $H_2O_2$. In addition, the temperature coefficients were easily reproducible.

When $Li_2O$ is added to NiO and fired in air the final product has adsorbed oxygen to such an extent that the $Ni^{3+}$ content is equivalent to the amount of lithium added to the system (De Boer and Verwey, 118). Thus:-

$$\tfrac{1}{2}\,x\,Li_2O + (1-x)\,NiO + \tfrac{1}{4}\,x\,O_2 = (Li_x^{2+}Ni_{1-2x}^{3+}Ni_x^{3+})O.$$

x = fraction NiO replaced.

The concentration of positive holes will increase with increasing lithium addition. It can be seen from Fig. 41 that the catalyst efficiency in this reaction increased as the $Li^+$ content increased, i.e. with increasing p-type character of the oxide, and consequently as electron interaction sites become more readily available to initiate reaction. This explanation would appear to fit the experimental data, adds weight to the early activity series (section (2) ), and also to the postulate that the rate controlling step is electron interation between catalyst and substrate. The NiO + $Li_2O$ catalysts may then be better than "green" NiO through the greater availability and reactivity of electron sources such as $O^-$ or $O_2^-$ with which this surface will be permanently saturated.

As to the instability of the "black" NiO, containing no $Li^+$, it may be stated that the latter cannot be considered to be a stable or specific structure. The oxygen content varies with the manner and temperature of its preparation, and although the present catalyst was specified by X-ray, magnetic and chemical analysis, its exact composition could only be duplicated by rigorous repetition of the experimental procedure. Thus though the "black" catalyst is initially more active than any containing $Li_2O$, it soon worsens on exposure to $H_2O_2$ as $O^-$, $O_2^-$ and p holes are reduced superficially.

We may accept that as a result of the mechanical mixing, grinding and thermal treatment accorded to the impurity series, a uniform distribution is achieved in the lattice and the induced valency changes would be distributed throughout the bulk. So that it may be considered that whilst "black" NiO loses

efficiency through the loss of excess surface oxygen, $NiO + Li_2O$ is stable since the excess oxygen is balanced throughout the lattice by an equivalent number of vacant cation sites and quasi-free positive holes giving a stable structure.

The decrease of the experimental $E_A$ on $NiO + Li_2O$ as the $Li^+$ content is increased may be explained on the same basis as that used above to describe the increase of efficiency. On the other hand, the effect on the catalysis of adding $Ga^{3+}$ is difficult to interpret. The first effect is to mop up already existing positive holes in NiO, thus:-

$$2 \oplus + Ga_2O_3 = 2\ Ga^+ (Ni) + 2\ NiO + \tfrac{1}{2}O_2(g)$$

where $\oplus$ = positive hole.

All the mixtures containing $Ga_2O_3$ were pale green in colour and did not alter during contact with $H_2O_2$. The samples containing 0.004 mol % $Ga_2O_3$ showed exactly the same activity at 60-138°C as the "green" nickel oxide, which leads to the conclusion that the impurity concentration was not great enough to appreciably modify the Fehlordnung of NiO, at any rate as far as the catalysis was concerned. Further addition of $Ga^{3+}$ did not, as may be expected, produce the opposite effect to that of $Li^+$, in that the catalyst efficiencies did not decrease steadily with increasing $Ga^{3+}$, but increased to a fairly constant level independant of the amount of $Ga_2O_3$ added. This level was about 1.5 times as high as pure NiO and the same as for NiO containing 0.24 mol % $Li_2O$.

On the other hand, the experimental activation energies for the fast temperature changes for the $Ga_2O_3$ series were found to increase with $Ga^{3+}$ content from 7 to 12 K.cals/mol for a T drop from 100 to 58°C, and to remain fairly steady at 6 ± 1 K.cals/mol for a T rise from 58 to 136°C. It may be

that as with CuO, there is a possibility of a surface reduction by $H_2O_2$ upsetting the distribution of electronic surface defects giving $Ni^+$ which may then readily initiate the reaction by losing an electron to an adsorbed $H_2O_2$ molecule. This cannot be considered very feasible, however, as it would not account for the inferiority of NiO as a catalyst; nor can the existence of $Ni^+$ be considered probable. However, it may be supposed that the increase in quasi-free electron concentration by adding $Ga_2O_3$ will not only annihilate certain positive holes but, in many cases, will lead to the formation of excitons (An exciton is produced when an electron is trapped in the electrostatic field of a positive hole, Frenkel, 166). These would be potentially low energy source of electrons and could initiate decomposition by electron transfer to an adsorbed $H_2O_2$ molecule giving a high efficiency at 100°C (say). Then when the temperature is dropped to 58°C, the surface is momentarily poisoned by an excess of $OH^-$ or $O_2$ (ads.) giving a low rate and a high $E_A$. After about 25 minutes, the equilibrium is reestablished and the rate recovers to a higher efficiency. Then, on raising the temperature to 136°C the decomposition rate gives a steady high value almost instantaneously, due to the absence of $OH^-$ poisoning or faster $O_2$ desorption. The catalyst is then similar in activity to "green" NiO and for the fast T change gives an identical $E_A$.

(8) Catalysis on equimolar mixed oxides.

Early practical applications of catalysts for decomposing concentrated liquid $H_2O_2$ made use of mixed Pb, Mn, Fe and Cu oxides in a matrix of cement made highly alkaline with KOH, but the influence of composition and treatment was only vaguely understood, and does not appear to have been investigated.

This choice of the above oxides could hardly have been improved, for, as we have seen, these are the most efficient catalysts for gas phase $H_2O_2$

destruction. What was not clear was what advantage, if any, was obtained from the simultaneous use of these active oxides; whether any synergesis was involved i.e. whether the catalytic action of a mixture of oxides was greater than the single oxides used separately. Such effects are, of course, common in heterogeneous catalysis e.g. in Fischer-Tropsch catalysts, in which mixtures of oxides very similar to these mentioned above have long been used. The decision to study the mixed oxides by the use of spinel-like mixtures was largely based on the availability of the studies Hüttig (73) had made of spinels. We chose the two series, one based on $Mn_2O_3$ and one on CuO, so as to focus attention separately on the divalent and trivalent ions.

In the $Mn_2O_3$ series we studied the effect of annealing temperature on the mixed oxides, and demonstrated that it is not the final spinel - like structure which is most active but the intermediate states which give the best catalysts. Thus, as would be expected, it is the most highly distorted crystals which are most active. Following Hüttig's discussion, we conclude that the most active mixture is that which is heated to the point where migration of foreign ions into neighbouring crystallities in a mixture has begun. At this point, which seems to be at 600°C for all the $Mn_2O_3$ mixtures, the number and variety of lattice imperfections will probably be greatest, though in the absence of a very full study of semi-conductivity it is not possible to be precise about this. As was shown in the X-ray and paramagnetic work, considerable structural alterations were induced by sintering, and these appear to be related to catalytic efficiency.

The qualitative results obtained when these catalysts were used to decompose liquid H.T.P. showed that the best gas phase catalysts were also superior in the aqueous phase.

The onset of ferromagnetism was not observed with all the equimolar mixtures based on $Mn_2O_3$ but susceptibility changes were, and may be attributed to the changes in the magnetic environment of diffusing paramagnetic ions over the surface, and perhaps also to valence induction (Anderson, 167). The loss of catalytic activity coincides with the destruction of the labile intermediate states of the mixed oxides and the formation of a more stable structure at high (700-800°C) temperatures of sintering. The active centres will then have a lower activity and this may explain why the activities of the mixed $Mn_2O_3$ catalysts steadily increased in the 300°C, 400°C and 600°C series, and then showed a marked fall with the 720 or 760°C preparations.

With the $Mn_2O_3$ series no very striking effect of adding a second oxide was observed. This was probably due to the very high activity of $Mn_2O_3$ itself ($E_A$ = 6.9 K.cals/mol and 100% decomposition at 80°C for the 600°C sinter). It was at first sight surprising that the ZnO mixtures did not show a bigger fall in activity compared with $Mn_2O_3$ itself. We must infer that even at 400°C, there is some surface migration so that the sample exhibits almost as many active sites as when it consists entirely of $Mn_2O_3$.

A striking result with the $Mn_2O_3$ mixtures is the marked enhancement of catalysis brought about in the $ZnO/Mn_2O_3$ series when more fully annealed. The inactive n-type oxide definitely induces an outcrop of new and active sites. These new sites could arise either in the $Mn_2O_3$ or ZnO crystals by introduction of impurities, or alternatively at interfaces between the p and n-type crystals, which would appear to provide excellent sites for the type of dual site cyclic catalysis which seems most likely to be involved, and which we have already postulated.

Apart from the case of the $ZnO/Mn_2O_3$ mixtures, this $Mn_2O_3$ group offers

little of striking interest from the catalytic viewpoint.

The mixtures based on CuO, an n-type oxide of intermediate activity, were more interesting, especially when the second oxide is $Fe_2O_3$ or $Al_2O_3$, though here again when the active $Co_2O_3$ was used its high activity seemed to obscure any mixture effect. These mixtures all gave strikingly lower $E_A$ values than the separate oxides and were much more catalytic. Like the single oxides and metal/metal oxides examined, they all conformed to the general pattern, already discussed, of slightly higher $E_A$ value with increasing temperature of the catalyst (The $Mn_2O_3$ mixtures in some cases did not conform to this behaviour). CuO . $Co_2O_3$ had an average $E_A$ = 4.0 K.cals/mol in the region 39-100°C; CuO. $Fe_2O_3$ had $E_A$ (avg.) = 8.5 K.cals/mol in the same temperature range; CuO. $Al_2O_3$, active in the 140-179°C range, gave $E_A$ = 15 K.cals/mol, and unlike $\alpha$-$Al_2O_3$ showed no tendency to lose activity on exposure to $H_2O_2$.

We may consider the $Co_2O_3$/CuO and $Al_2O_3$/CuO mixtures to be similar to the $Mn_2O_3$/NiO specimens in that solid solutions of the two oxides would be formed giving an active surface with many possible electron sources to initiate decompositions (see section 4(d) of results). On the other hand, CuO readily forms a spinel with $Fe_2O_3$ (Forestier, 117) and at the temperature of preparation (600°C) may form a complex structure with some inversion of the position of di and trivalent ions yielding a highly defect structure which is so effective in catalysis when compared with the individual oxides. This provides a plain case of synergism and the effect may be to give rise to sites requiring a lower $E_A$ than present in either oxide. Again, as in the case of ZnO/$Mn_2O_3$, it may be the junction between the crystals which produces the most active catalysis. The alumina mixtures provide the sole example of a diluent effect and can be explained if the alumina is able to poison the most active sites

on the CuO.

As stated earlier in this section, until more is known of the precise electronic nature of these compounds, it is not possible to invoke a precise description of the surface process without using tenuous arguments. What does emerge from this equimolar work is that a combination of two p-type oxides or two n-type oxides gives a better catalytic performance than the individual oxides, whilst a combination of n + p or n + insulator oxides is generally as good, but not much better, a catalyst than the better of the two individual components.

(9) Surface area and magnetic measurements.

Regarding the surface areas it may justifiably be concluded that as long as the roughness factors of a given series do not vary much, i.e. by a factor of 0.5-2, surface area measurements will not be of much significance unless some correlation can be made between this and the "active" area; which is difficult to achieve experimentally.

As regards the actual method used to find the surface areas, it was felt that the point "B" method would suffice to give the required data and this, of course, involves an error of selection of "B". However, as has been pointed out by Halsey (169) and Jacobs and Tompkins (168), the B.E.T. plot of $p/v(p_o-p)$ against $p/p_o$ is now regarded as simply a convenient method for locating "B" and, in fact, Tompkins considers it to be less valid than the method used in this work. The actual surface area results obtained here are regarded merely as providing evidence for the similarity in roughness of the catalysts examined.

The original object in studying the magnetic susceptibility was that it

was hoped to follow susceptibility change, if any, during catalysis, and the apparatus was constructed with this in mind. However, it was soon apparent that such an investigation would itself be a long-term project, and it would not be possible to accomplish this whilst making a kinetic investigation of a number of catalysts.

The magnetic susceptibilities were then used to determine sample purity and to give an indication of structural changes induced by progressive sintering. The results proved to be very useful in this respect.

The magnetic susceptibility of $Mn_2O_3$ was found to be $89.0 \times 10^{-6}$ cgs. units per gm., or $5.0 \times 10^{-3}$ cgs. units per gm. ion of manganese. With addition of equimolar ratios of a divalent diamagnetic ion the susceptibility for manganese ion was increased, e.g. with lead oxide (300°C) the value is $8.06 \times 10^{-3}$ and for ZnO addition the peak value reached at 600°C was $11.74 \times 10^{-3}$ cgs. units. These high values were sharply decreased when the temperature of treatment was high enough for sintering. Thus at 760°C the $ZnO/Mn_2O_3$ susceptibility had fallen to $4.26 \times 10^{-3}$ cgs. units per Mn ion.

Paramagnetic susceptibility is associated with electrons of unpaired spin. $Mn^{3+}$ has 4 (3d) electrons which would be unpaired, $Mn^{++}$ has 5, and $Mn^{4+}$ has 3. An increase of susceptibility per Mn ion must be considered to arise from reactions in which the diamagnetic oxide gains or loses an electron permitting a contribution to the total susceptibility. These unpaired electrons may not necessarily be associated with the metal ions but attached to ionic vacancies, e.g. as F - centres held in the diamagnetic oxide. On the other hand, simple donation of an electron from an interstitial position to $Mn^{3+}$ could occur, converting it to the more susceptible $Mn^{++}$.

Again, in the absence of a complete analysis of an oxide system as a semi-conductor in order to identify lattice and electron imperfections and the energy levels of trapped electrons or positive holes; the relationship between magnetic susceptibility and catalysis can only be considered in a qualitative manner. Among the best catalysts of the $AO/Mn_2O_3$ series were those with the highest paramagnetic susceptibility, i.e. the highest concentration of unpaired electrons per Mn ion, e.g. $PbO/Mn_2O_3$ at 300°C and $ZnO/Mn_2O_3$ at 600°C. These unpaired electrons are clearly associated with catalytically active sites but susceptibility measurements tell nothing of the stability or reactivity of these sites. Some highly susceptible oxides may have a high proportion of the unpaired electrons in tightly held and non-reactive positions, and therefore be poor catalysts. However, it is quite clearly established that susceptibility measurements are a useful quide to the effect of temperature and other pre-treatments in affecting catalytic properties; especially when dealing with oxides of closely related types.

(10) Conclusion.

This thesis describes work which has, for the first time, been directed towards elucidating the mode of decomposition of hydrogen peroxide vapour on a wide range of metallic oxide surfaces in a flow system. The results show that there appears to be a link between catalyst efficiency and electronic structure of the oxides examined. To this end, modifications of the Fehlordnung of nickel oxide by the addition of alter-valent ions has yielded substantive data.

In addition, the kinetics of the decomposition have been evaluated showing the dependance of the reaction rate on the decomposition products. A possible reaction mechanism and rate-determining step have been proposed.

Certain physical and structural properties have been investigated and the results critically applied to appraise the nature of certain catalyst systems whose preparations were closely controlled. Emphasis has been laid on the necessity of having adequate knowledge of the previous history of a catalyst in order to obtain reproducible results and on the essential need to excercise care in selecting cleaning fluids.

It is felt that the information emerging from this work will contribute to our expanding knowledge of catalyst surface processes, which have been rather neglected in the past, when most attention has been directed at evaluating the gas phase kinetics. Certain aspects, like semi-conductivity and magnetic susceptibility changes of the catalyst during reaction, will bear investigation and it is hoped that these avenues when fully explored will add further to our knowledge of heterogeneous catalysis.

REFERENCES

(1) Thénard, Ann. Chim et phys., 1818, 8, 306.

(2) Thénard, Mem. Acad. Sci., Paris, 1818, 3, 345.

(3) Thénard & Thénard, Compt. rend., 1855, 41, 341.

(4) Thénard & Thénard, Ann. Chim et phys., 1856, 47, 173.

(5) Bredig, "Anorganische Fermente", Engelmann, Leipzig, 1901.

(6) Teletof, I.S. & Gritsan, Bull. Khim. Obshchestva im Mendeleeva, 1940, 8, 22 (Chemical Abstracts 37, 3659).

(7) Seitz, Revs. Mod. Phys. 1946, 18, 384.

(8) Haber & Willstäter, Ber., 1931, 64, 2844.

(9) Haber & Weiss, Proc. Roy. Soc. A., 1932, 147, 332.

(10) Baxendale, Evans & Park, Trans. Far. Soc., 1946, 42, 155.

(11) Dainton, J. Phys. & Colloid. Chem., 1948, 52, 490.

(12) Barb, Baxendale, George & Hargrave, Trans. Far. Soc., 1951, 47, 462.

(13) Weiss, Far. Soc. Disc., 1947, 2, 212.

(14) Evans, Hush and Uri, Quart. Revs. Chem. Soc., 1952, 4, 186.

(15) Baxendale, Evans & Uri. Trans. Far Soc., 1949, 45, 236.

(16) Weiss, ibid, 1935, 31, 1547.

(17) Dowden & Reynolds, Far. Soc. Disc., 1950, 8, 184 .

(18) Wiegel, Z. Phys. Chem., 1929, 143A, 81.

(19) Broughton & Wentworth, J. Amer. Chem. Soc., 1947, 69, 741.

(20) Broughton, Wentworth & Farnsworth, ibid., 1949, 71, 2346.

(21) Voltz & Weller, ibid., 1954, 76, 1586.

(22) Mooi & Selwood, ibid, 1952, 74, 1750.

(23) Schwab, La Chimica e Industria, 1953, 35, 810.

REFERENCES (Continued)

(24) Hart, Nature, 1949, 163, 876.

(25) Satterfield, Ceccotti & Feldbrugge. Ind. Eng. Chem., 1950, 47, 1040.

(26) Satterfield, and Stein, J. Phys. Chem., 1957, 61, 537.

(27) Hauser, Ber., 1923, 56, 888.

(28) Hinshelwood & Pritchard, J. Chem. Soc., 1923, 123, 2725.

(29) Elder & Rideal, Trans. Far. Soc., 1927, 23, 545.

(30) Rosenberg & Kistiakowsky, J. Amer. Chem. Soc., 1937, 59, 422.

(31) Reuter & Gaukhman, J. Phys. Chem. (U.S.S.R.), 1933, 4, 465.

(32) Mackenzie & Ritchie, Proc. Roy. Soc. A., 1946, 185, 207.

(33) Baker & Ouellet, Can. J. Res., 1945, 23B, 167.

(34) Giguère, ibid, 1947, 25B, 135

(35) McLane, J. Chem. Phys., 1949, 17, 379.

(36) Harris, Trans. Far. Soc., 1948, 44, 764.

(37) Giguère & Liu, Can. J. Chem., 1957, 35, 283.

(38) Mott & Gurney, "Electronic Processes in Ionic Crystals", Oxford, 1950.

(39) Schockley, "Electrons & Holes in Semi-Conductors", van Nostrand, New York, 1951.

(40) Anderson, Ann. Reps. Chem. Soc., 1946, 43, 104.

(41) Cabrera & Mott, Rep. Prog. Phys., 1949, 12, 163.

(42) Wagner, J. Chem. Phys., 1950, 18, 62.

(43) Gray, "Chemistry of the Solid State", ed. Garner, Butterworths, London, 1955, pp.133.

(44) Garner, Stone & Tiley, Proc. Roy Soc. A., 1952, 211, 472.

(45) Dell, Stone & Tiley, Trans. Far. Soc., 1953, 49, 201.

REFERENCES (Continued)

(46) Garner, Gray & Stone, Far. Soc. Disc., 1950, 8, 246.

(47) Garner, Gray & Stone, Proc. Roy. Soc. A., 1949, 197, 294.

(48) Wagner & Hauffe, Z. Electrochem., 1938, 44, 172.

(49) Gray, Proc. Roy. Soc. A., 1949, 197, 314.

(50) Gray & Savage, Far Soc. Disc., 1950, 8, 250.

(51) Hauffe, Glang & Engell, Z. Phys. Chem., 1952, 201, 223.

(52) Dell & Stone, Trans. Far. Soc., 1954, 50, 501.

(53) Parravano, J. Amer. Chem. Soc., 1953, 75, 1448.

(54) Parravano, ibid, 1953, 75, 1452.

(55) Schwab & Block, Z. Phys. Chem., (N.F.)., 1954, 1, 42.

(56) Stone, ref. (43) pp.399.

(57) Verwey, "Semi-Conductors", Butterworths, London, 1951, pp.151.

(58) Wagner, J. Chem. Phys., 1950, 18, 69.

(59) Molinari & Parravano, J. Amer. Chem. Soc, 1953, 75, 5233.

(60) Heckelsberg, Clark & Bailey, J. Phys. Chem., 1956, 60, 559.

(61) Parravano, J. Amer. Chem. Soc., 1952, 74, 1194.

(62) Gray & Darby, J. Phys. Chem., 1956, 60, 209.

(63) Pink, Ann. Reps. Chem. Soc., 1949, 46, 34.

(64) Emmett, "Catalysis I", Reinhold, New York, 1954, pp.31.

(65) Hüttig, Kolloid - Z., 1941, 94, 258.

(66) Hüttig, ibid, 1942, 95, 262.

(67) Selwood, Chem. Revs., 1946, 38, 41.

(68) Selwood, ref. (64), pp.353.

(69) Selwood, Moore, Ellis & Wethington, J. Amer. Chem. Soc., 1949, 71, 693.

REFERENCES (Continued)

(70) Selwood, Hill & Boardmann, ibid, 1946, 68, 2058.

(71) Stroupe, ibid, 1949, 71, 569.

(72) Hüttig, Funke & Kittel, ibid, 1935, 57, 2470.

(73) Hüttig, Far. Soc. Disc., 1950, 8, 215.

(74) Brunauer, Emmett & Teller, J. Amer. Chem. Soc., 1938, 60, 309.

(75) Emmett & Brunauer, ibid, 1937, 59, 1553.

(76) Duncan, Trans. Far. Soc., 1949, 45, 879.

(77) Wooten & Callaway - Brown, J. Amer. Chem. Soc., 1943, 65, 113.

(78) Taylor, H.S., ibid, 1931, 53, 578.

(79) Volkenshtein, Zhur. Fiz. Khim, 1949, 23, 917.

(80) Boudart, J. Chem. Phys., 1950, 18, 571.

(81) Hart & Mc.Fadyen, In course of publication, Glasgow.

(82) Constable, Proc. Roy. Soc. A., 1925, 108, 355.

(83) Farkas & Melville, "Experimental Methods in Gas Reactions", McMillan, London, 1939, pp. 102.

(84) Kavanagh, Scatchard, and Ticknor, J. Amer. Chem. Soc. 1952, 74, 3715.

(85) Finch, Quarrell & Wilman, Trans. Far. Soc., 1935, 31, 1051

(86) Trapnell, ibid, 1955, 51, 368.

(87) Sucksmith, Phil. Mag., 1929, 8, 158.

(88) Dilke, Eley & Maxted, Nature, 1949, 161, 804.

(89) Beeck, Smith & Wheeler, Proc. Roy. Soc. A., 1941, 177, 67.

(90) Tyrer, J. Chem. Soc., 1911, 99, 1633.

(91) Giguère & Geoffrion, Can. J. Res., 1949, 27B, 168.

(92) Easton, Mitchell & Wynne - Jones, Trans. Far. Soc., 1952, 48, 796.

REFERENCES (Continued)

(93) Nelson, J. Chem. Phys., 1937, 5, 252.

(94) Rhodin, J. Amer. Chem. Soc., 1950, 72, 5102.

(95) Ref. 38, pp.262.

(96) Nettleton, Thesis, Royal College of Science & Technology, Glasgow, 1953.

(97) Hüttig & Heinz, Z. Anorg. Chem., 1948, 255, 223.

(98) Nizboer, Proc. Phys. Soc., 1939, 51, 575.

(99) Leblanc & Sachse, Z. Electrochem., 1926, 32, 59 & 204.

(100) Rooksby, Nature, 1943, 152, 304.

(101) Bennett, Cairns & Ott, J. Amer. Chem. Soc., 1931, 53, 1179.

(102) Day & Hill, J. Phys. Chem., 1953, 57, 946.

(103) Howell, Proc. Roy. Soc., 1923, 104, 134.

(104) Suhrmann & Schulz, Z. Phys. Chem., (N.F.), 1954, 1, 69.

(105) Rideal & Trapnell, Proc. Roy. Soc. A., 1951, 205, 409.

(106) Rhodin, J. Amer. Chem. Soc., 1951, 73, 3143.

(107) Klemm & Hass, Z. Anorg. Chem., 1934, 219, 82.

(108) Selwood, "Magnetochemistry", Interscience, New York, 1956, pp.313.

(109) Howell, J. Chem. Soc., 1923, 123, 669.

(110) Finch & Sinha, Trans. Far. Soc., 1957, 53, 623.

(111) Bhatnagar & Bal, J. Ind. Chem. Soc., 1934, 11, 603.

(112) Perakis, Serres, Parravano & Wucher, Compt. Rend., 1956, 242, 1275.

(113) Wells, "Structural Inorganic Chemistry", Oxford, 1950, pp.381.

(114) Greenwald, Pickart & Grannis, J. Chem. Phys., 1954, 22, 1597.

(115) Gorgeu, Bull. Soc. Chim., 1903, 29, 1111.

(116) Castell, Dilnot & Warrington, Nature, 1944, 153, 653.

REFERENCES (Continued)

(117) Forestier, Compt. Rend., 1931, 192, 842.

(118) De Boer & Verwey, Proc. Phys. Soc., 1937, 49, 59.

(119) Fensham, J. Amer. Chem., 1954, 76, 969.

(120) Schwab & Pietsch, Z. Phys. Chem., 1926, 121, 189.

(121) Palmer & Constable, Proc. Roy. Soc. A., 1924, 106, 250.

(122) Twigg, Trans. Far. Soc., 1946, 42, 284.

(123) Kulkova & Temkin, Zhur Fiz. Khim., 1949, 23, 695.

(124) Darby & Kemball, Trans. Far. Soc., 1957, 53, 832.

(125) Beeck, Far. Soc. Disc., 1950, 8, 118.

(126) Kemball, Proc. Roy. Soc. A., 1952, 214, 413.

(127) Couper & Eley, Far. Soc. Disc., 1950, 8, 118

(128) Dowden, J. Chem. Soc., 1950, 242.

(129) Trapnell, Proc. Roy. Soc. A., 1953, 218, 566.

(130) Gray and Darby, J. Phys. Chem., 1956, 60, 201.

(131) Boudart, J. Amer. Chem. Soc., 1952, 74, 1531.

(132) Weisz, J. Chem. Phys., 1953, 21, 1531.

(133) Taylor and Thon, J. Amer. Chem. Soc., 1953, 75, 2747.

(134) Twigg, Proc. Roy. Soc. A., 1948, 188, 92.

(135) Laidler, ref. (64) pp.190.

(136) Roberts, Proc. Roy. Soc. A., 1935, 152, 445.

(137) Trapnell, ibid, 1951, 206, 39.

(138) Smith and Taylor, J. Amer. Chem. Soc., 1938, 60, 362.

(139) Roginskii & Tselinskaya, Zhur. Fiz. Khim., 1948, 22, 1350.

REFERENCES (Continued)

(140) Tu, Davis and Hottel, Ind. Eng. Chem., 1934, 26, 749.

(141) Katz, Riberdy and Grant, Can J. Chem., 1956, 34, 1719.

(142) Satterfield, Resnick and Wentworth, Chem. Eng. Prog., 1954, 50, 460.

(143) Zimmerman, J. Phys. Chem., 1949, 53, 562.

(144) Riddiford, ibid, 1952, 56, 745.

(145) Dole, Rudd, Muchow and Comte, J. Chem. Phys., 1952, 20, 961.

(146) Brodie, Phil. Trans., 1863, 152, 837.

(147) Wright and Andrews, Proc. Phys. Soc., 1949, 446.

(148) Rideal and Wilkins, Proc. Roy. Soc. A., 1930, 128, 394.

(149) Mott, Trans. Far. Soc., 1940, 36, 472.

(150) Vernon, ibid, 1927, 23, 152.

(151) Hart, R.K., ibid, 1957, 53, 1020.

(152) Trapnell, Quart. Revs. Chem. Soc., 1954, 8, 404.

(153) Rideal and Trapnell, Far. Soc. Disc., 1950, 8, 114.

(154) Taylor and Liang, J. Amer. Chem. Soc., 1947, 69, 1306.

(155) Barrer, J. Chim. Phys., 1950, 47, 444.

(156) Cremer & Marschall, Monatsch, 1951, 82, 840.

(157) Mikovsky and Waters, quoted by Cremer, Advances in Catalysis, VII, Academic Press, New York, 1955, pp.81.

(158) Cremer, Advances in Catalysis VII, Academic Press New York, 1955, pp.75.

(159) Engell and Hauffe, Z. Electrochem., 1953, 57, 773.

(160) Temkin & Pyzhev, Acta Physicochim, 1940, 12, 327.

(161) Kwan, J. Res. Inst. Catalysis, 1953, 3, 16.

(162) Kwan, J. Amer. Chem. Soc., 1956, 60, 1033.

REFERENCES (Continued)

(163) Elovich & Zhabrova, Zhur. Fiz. Khim, 1939, 13, 1716, 1775.

(164) Stone, ref. (43), pp.385.

(165) Hinshelwood, "Kinetics of Chemical Change", Oxford, 1949, pp.216.

(166) Frenkel, Phys. Revs., 1931, 37, 1276.

(167) Anderson, Far. Soc. Disc., 1950, 8, 305.

(168) Jacobs & Tompkins, "Chemistry of Solid State", Ed. Garner, Butterworths, London, 1955, pp.95.

(169) Halsey, Far. Soc. Disc., 1950, 8, 54.